ZEROK NANOTECH

Ion Microscopy, Machining, and Elemental Analysis with the Cesium Low Temperature Ion Source (LoTIS)

M&M 2022
MICROSCOPY & MICROANALYSIS
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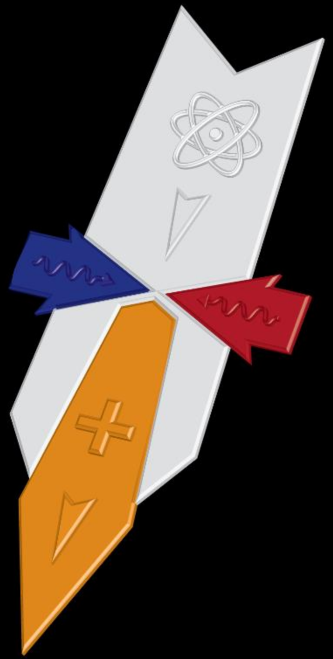
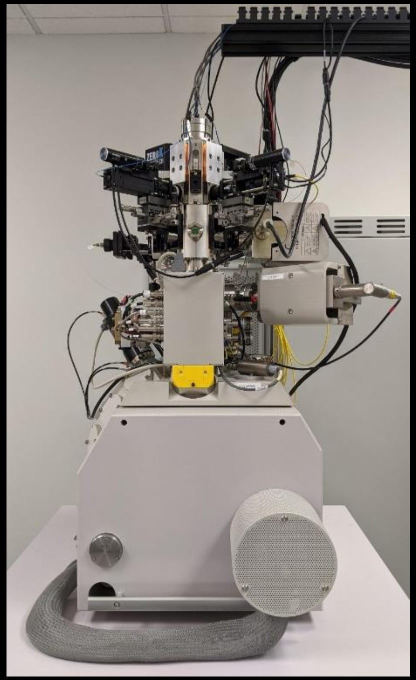
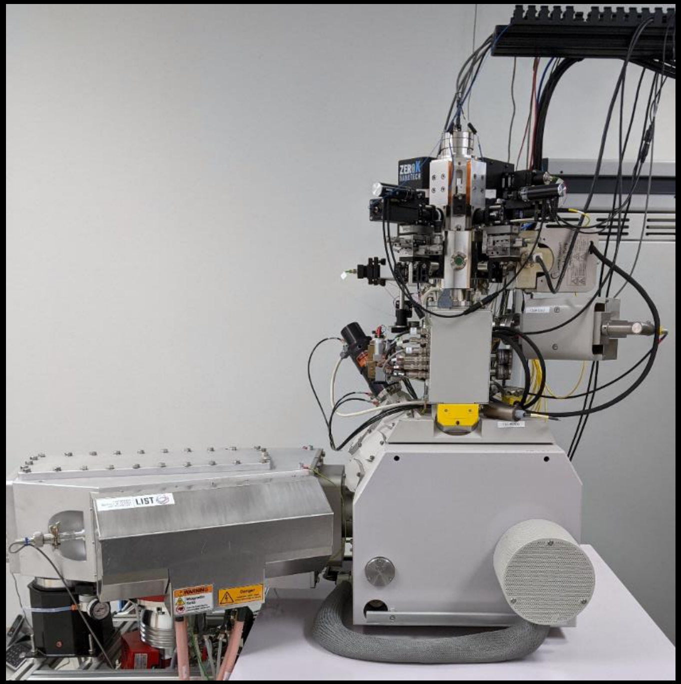
August 2022

Technology and Applications







Cs^+ LoTIS	FIB:ZERO	SIMS:ZERO

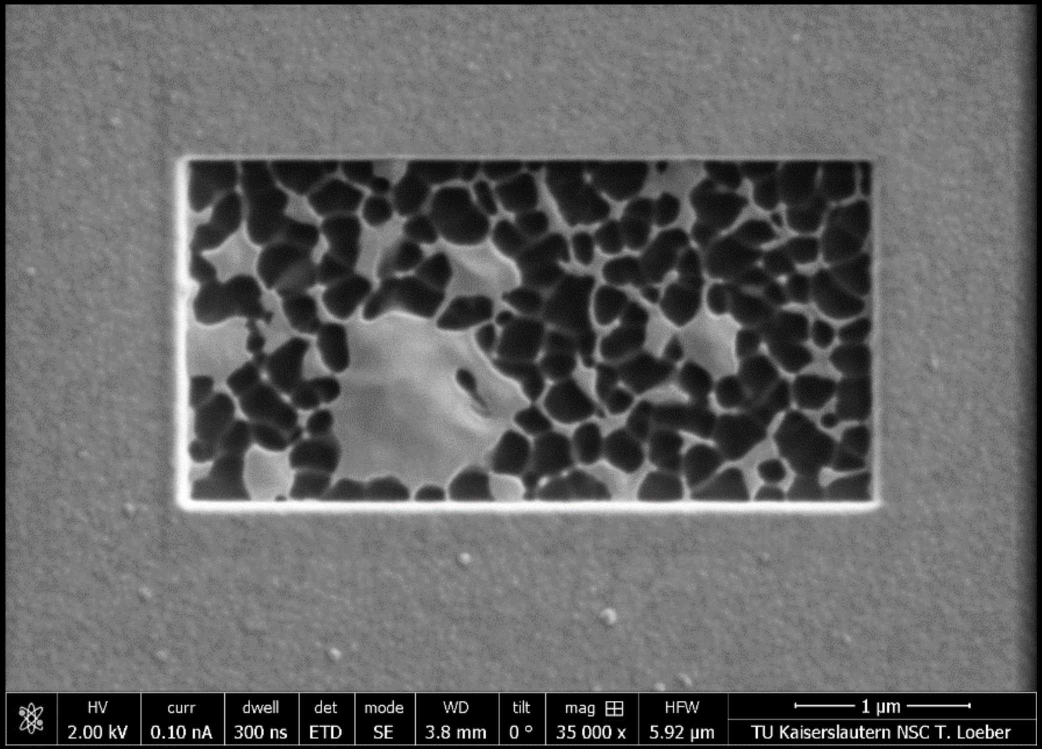
• Low Temperature Ion Source
  • Laser-cooling + Photoionization
• Heavy ion nanomachining
• Small spot sizes
• Excellent resolution at low energy (~2 nm resolution at 1 pA, 16 kV)
• 1 pA - 10 nA
	• LoTIS + FIB
	• Comparable to standard Ga^+ FIB, with 2x higher resolution at low beam currents
	• Compatible with normal peripherals, gas chemistries etc..
		• FIB:ZERO with SIMS
		  • Analysis of secondary ions in a mass spectrometer
		• Best for elemental-compositional analysis
		• Collab. with Luxembourg Institute of Science and Technology (LIST)

FIB:ZERO

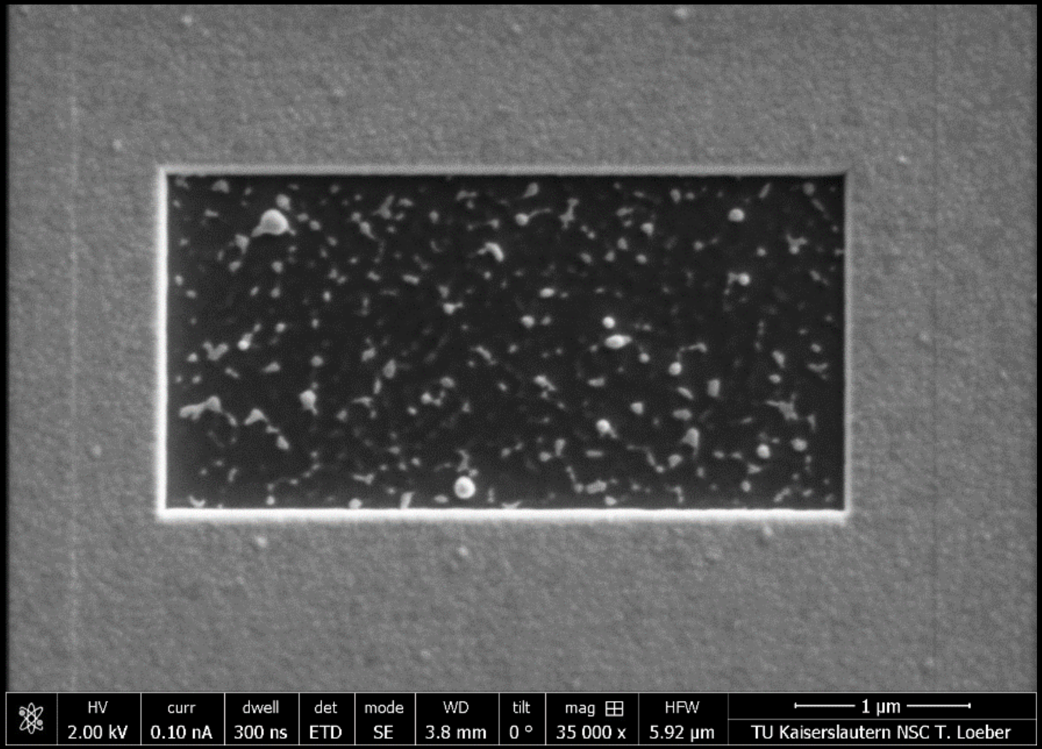
Milling Homogeneity: 150 nm Au on Si

→Cs^+ LoTIS proves even touchdown

Milled with Ga^+ LMIS



Milled with Cs^+ LoTIS

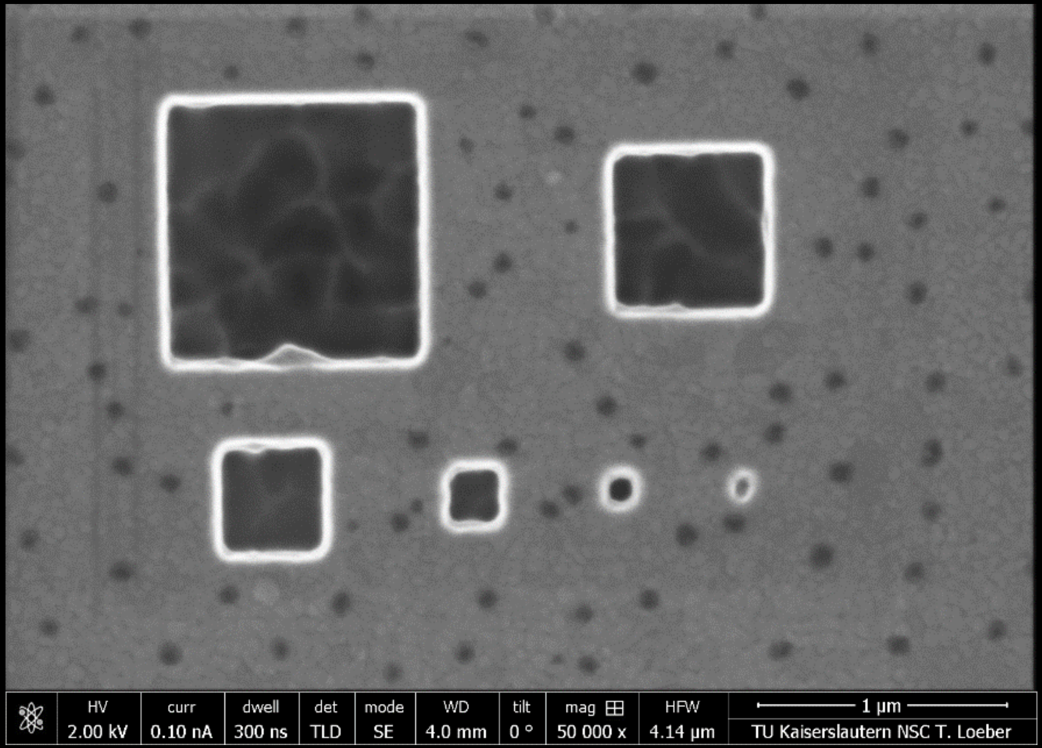


- milled rectangle ‘almost through’ the Au layer
- milling time Ga and Cs almost the same

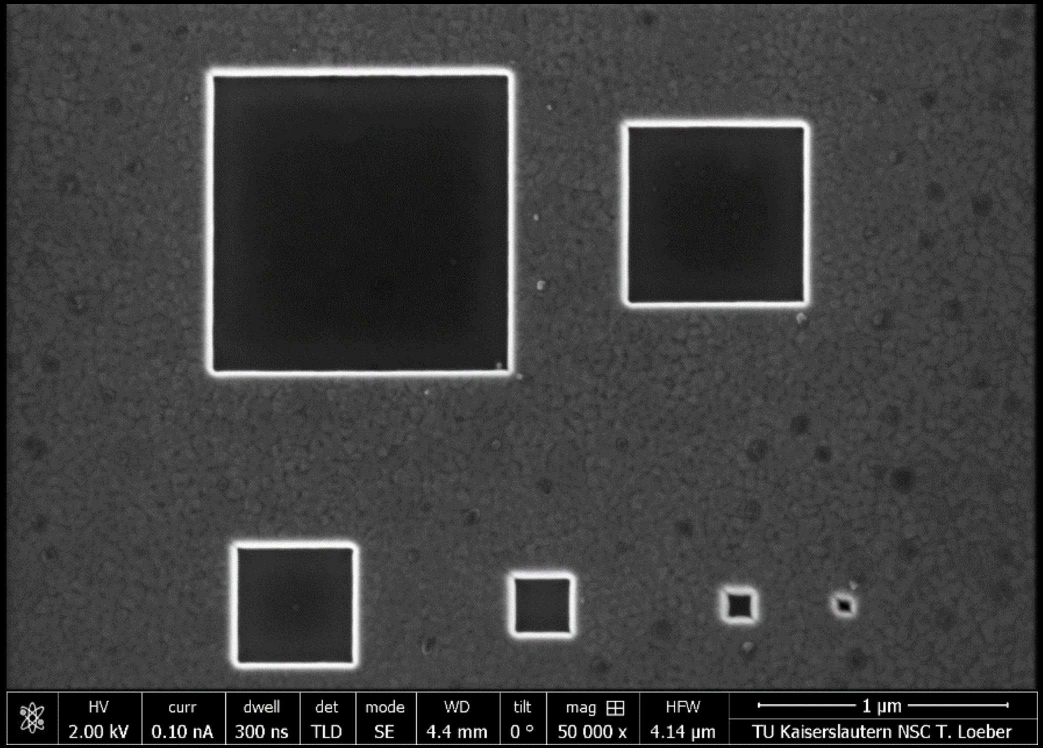
Milling Accuracy: 110 nm Au on Si

→ LoTIS provides clean mill boxes with sharp corners

Milled with Ga^+ LMIS



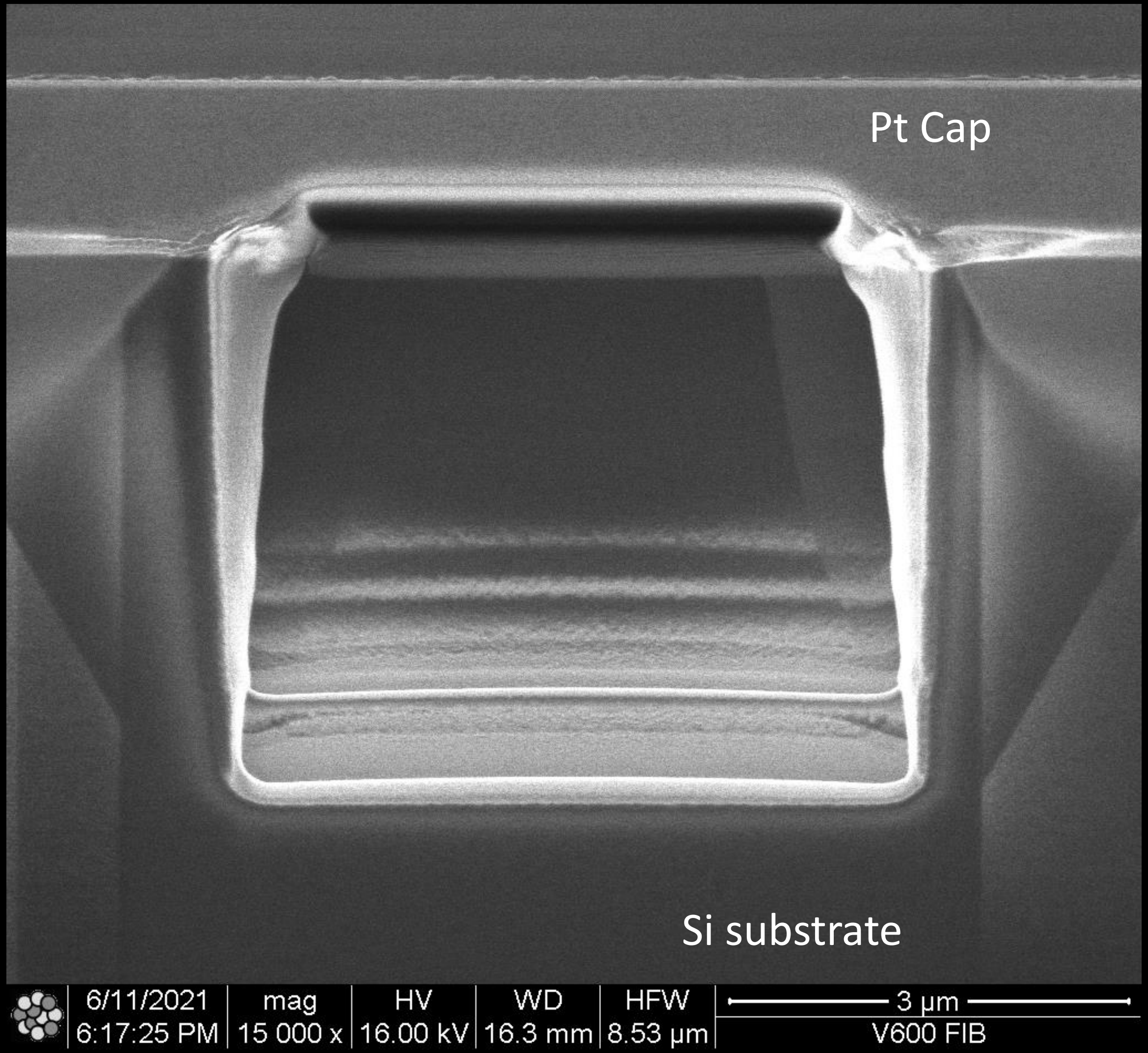
Milled with Cs^+ LoTIS

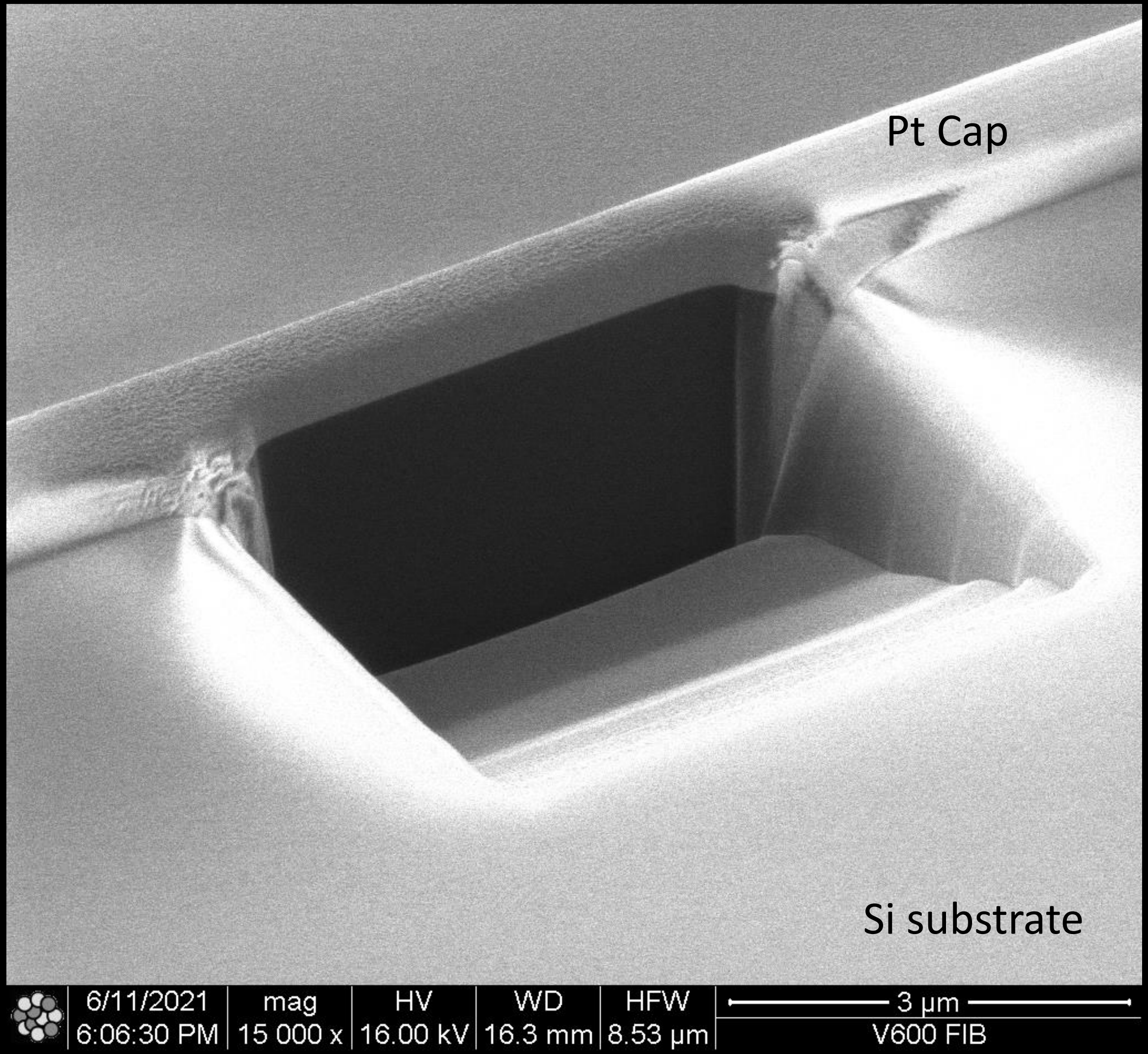


- squares with 1, 0.6, 0.4, 0.2, 0.1 and 0.05 µm length
- milled through the Au layer
- milling time Ga and Cs almost the same

FIB:ZERO Cross Section Example

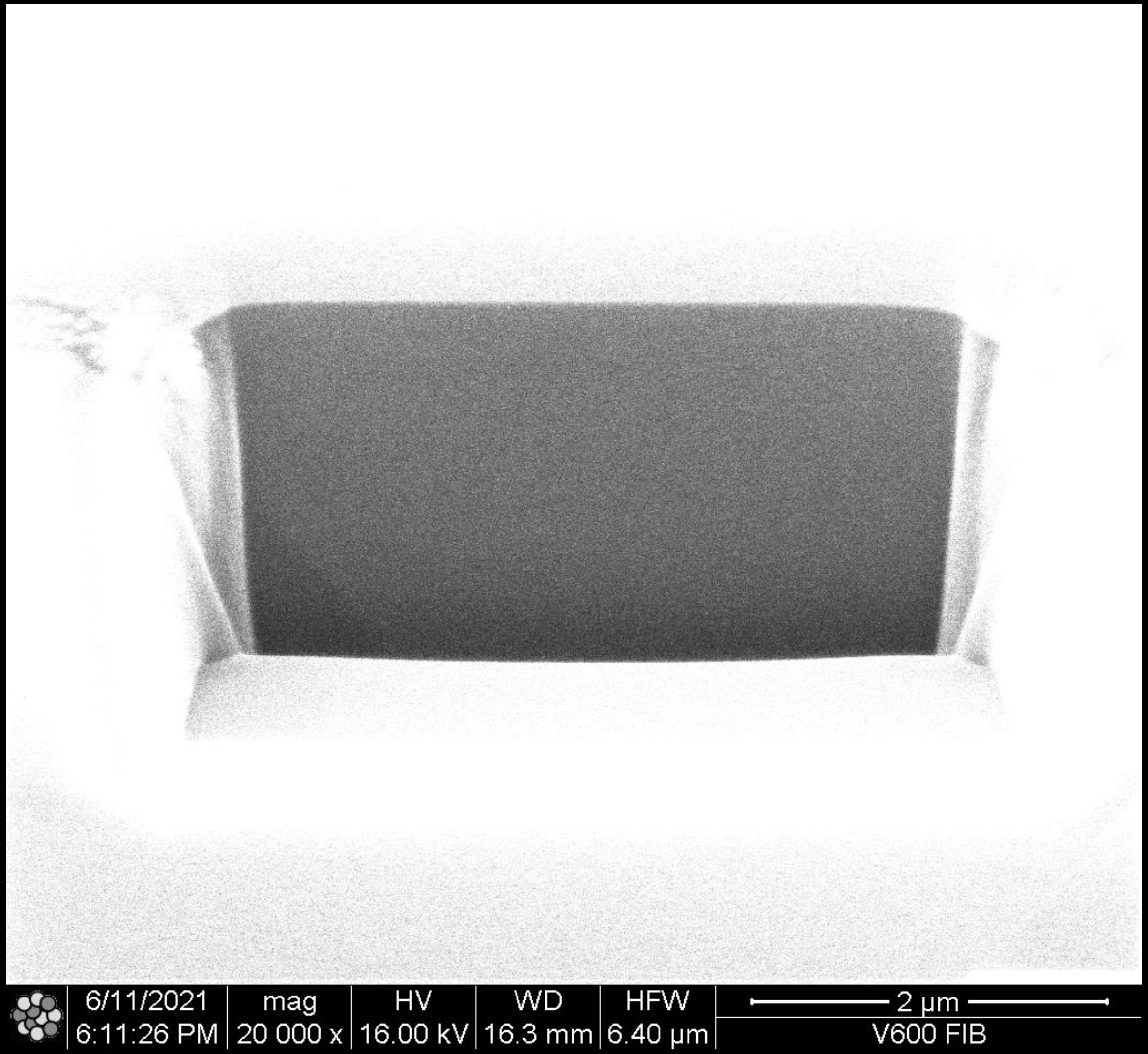
Done with 200 pA beam, 30 pA 'cleanup' afterwards

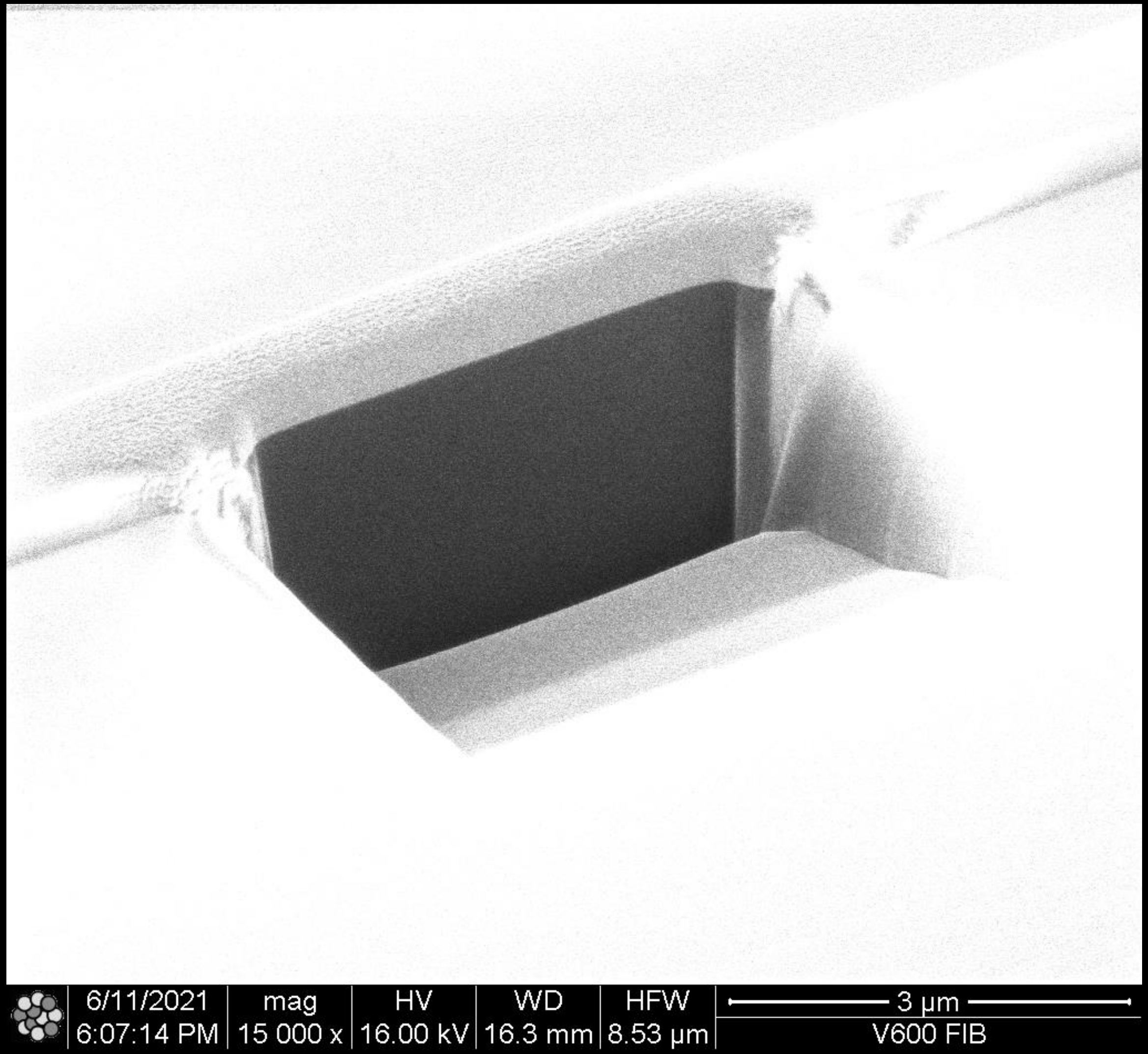




FIB:ZERO Cross Section Example

Oversaturated images to show lack of curtaining

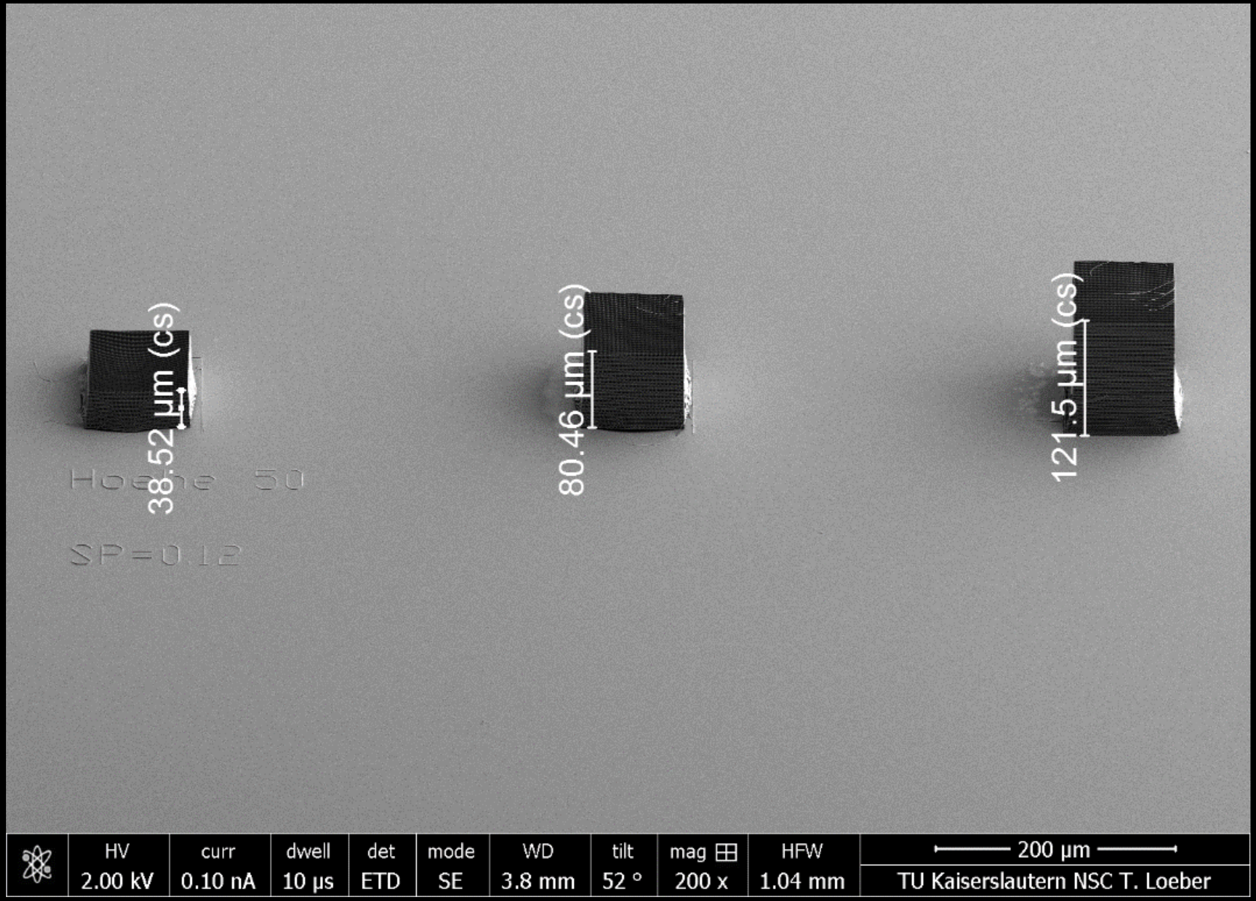




Depth of Focus Comparison

(Results on slides that follow)

FEI: SEM image



"Wood Pile" Nanostructures

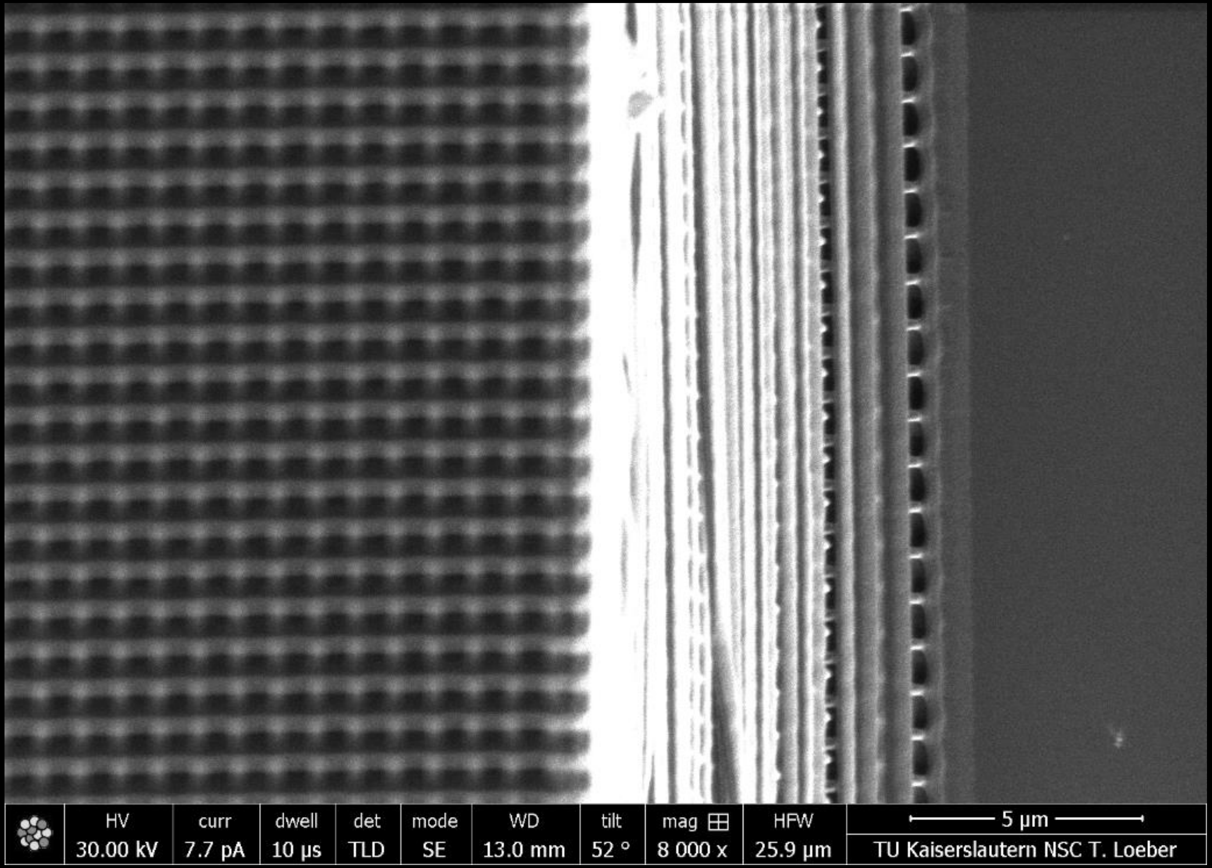
- Heights: 40 µm, 80 µm, 120 µm
- In the following slides we acquire an image containing both the top and bottom of such the 120 µm (tallest) structure
- We can compare the depth of focus of various beams by comparing the 'blurriness' of the top of the structure

A better depth of focus aids in the milling and imaging of 'deep' or 'tall' structures.

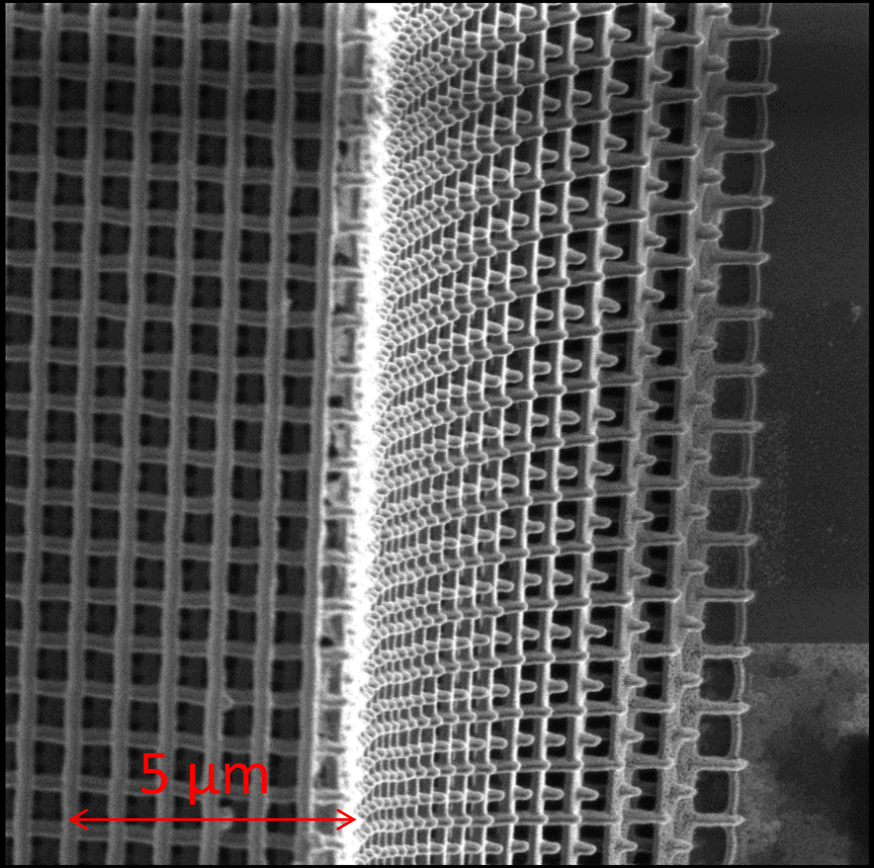
Depth of Focus Comparison

→LoTIS depth of focus substantially better than Ga

Ga⁺ LMIS (30 kV)



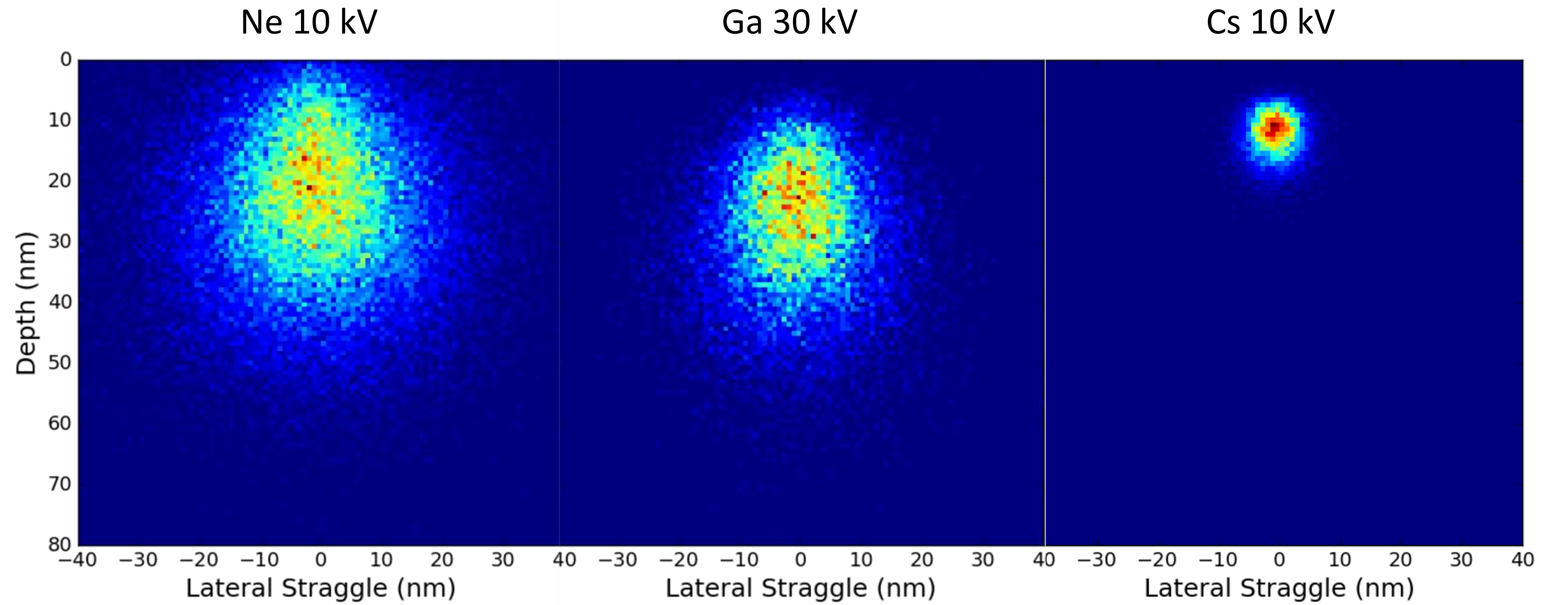
Cs⁺ LoTIS (10 kV)



"Wood Pile" Height 120 µm

Invaseness Comparisons (SRIM Calculations)

- Comparison of three scenarios where spot size might be 'good enough'
- Cs has significantly reduced straggle and implant depth



FIB:ZERO Milling Rates

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Milling rate of 10 kV Cs^+ FIB:ZERO about 15% lower than 30 kV Ga^+ for Si

Cs^+ LoTIS milling rates 90% higher than Ne^+ (and **much** higher than He^+)

Ne 10 kV	Ga 30 kV	Cs 10 kV
1.00-1.38 at/ion	2.20-2.40 at/ion	1.90-2.15 at/ion

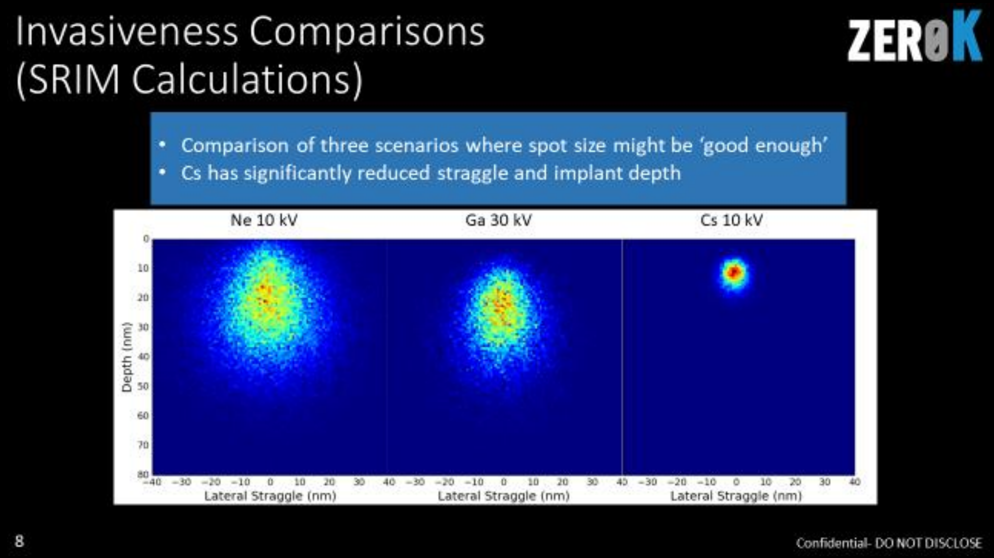
SUMMARY
FIB:ZERO

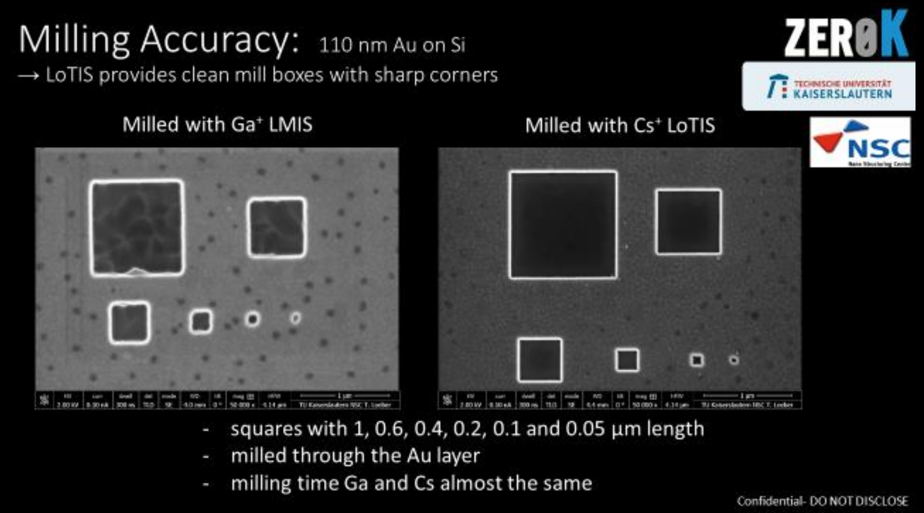
... is a ‘nanomachining’ tool

... has industry-leading performance at low beam currents and low energy

... is compatible with gas precursors for deposition or etch just like other FIBs

Data pictured right, implant depth and milling fidelity, summarize the story best





Pain Points of Existing Elemental Analysis Techniques and a New Solution

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EDX/EELS

- Long sample-prep times
- 3D analysis infeasible
- Low-Z elements challenging

Site-Specific SIMS

- Resolution limited to ~50 nm with high yield (CAMECA NanoSIMS), or
- Can get a high resolution FIB (Ga, He, Ne) with a time-of-flight SIMS analyzer. But low secondary ion yields from these beams usually results in poor lateral resolution. Additionally, time-of-flight analyzers necessitate **long** acquisition times.

These points are addressable by

SIMS:ZERO

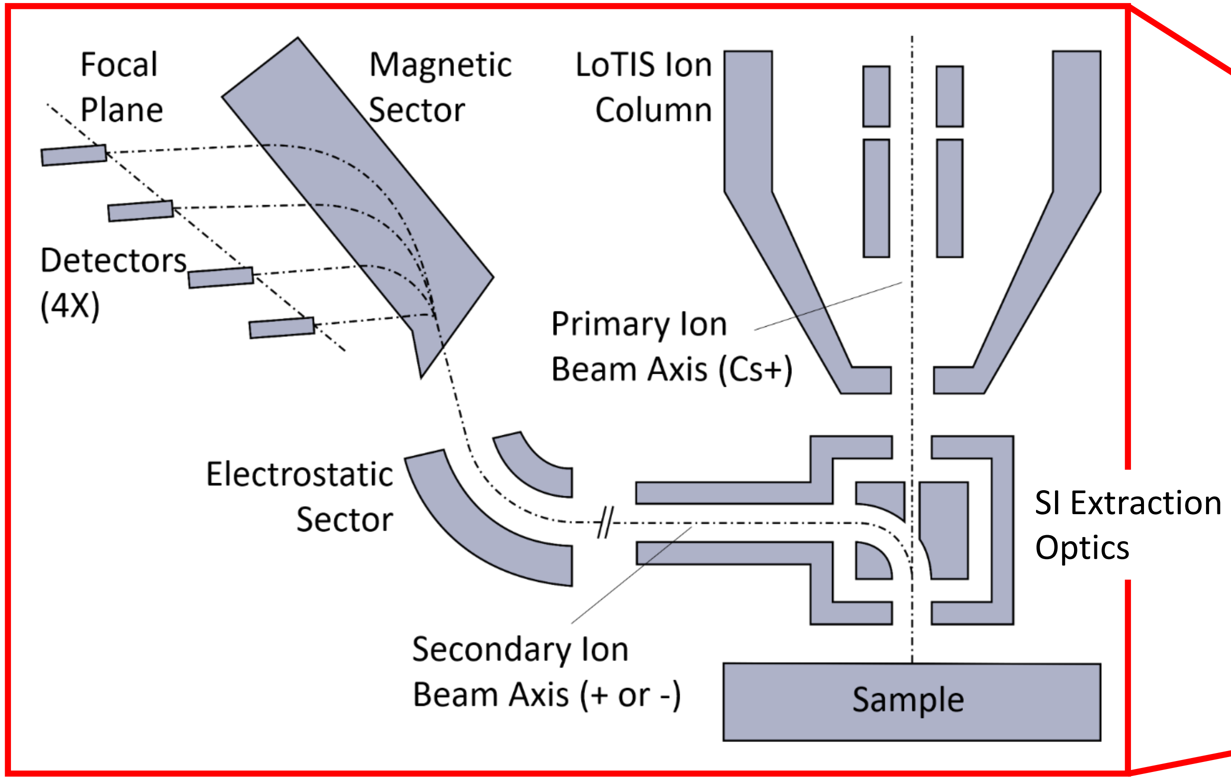
- Few-nanometer resolution (slide 21)
- High secondary ion yield (slides 23,24)
- Integrated sample-prep and analysis capability (slides 25-31)

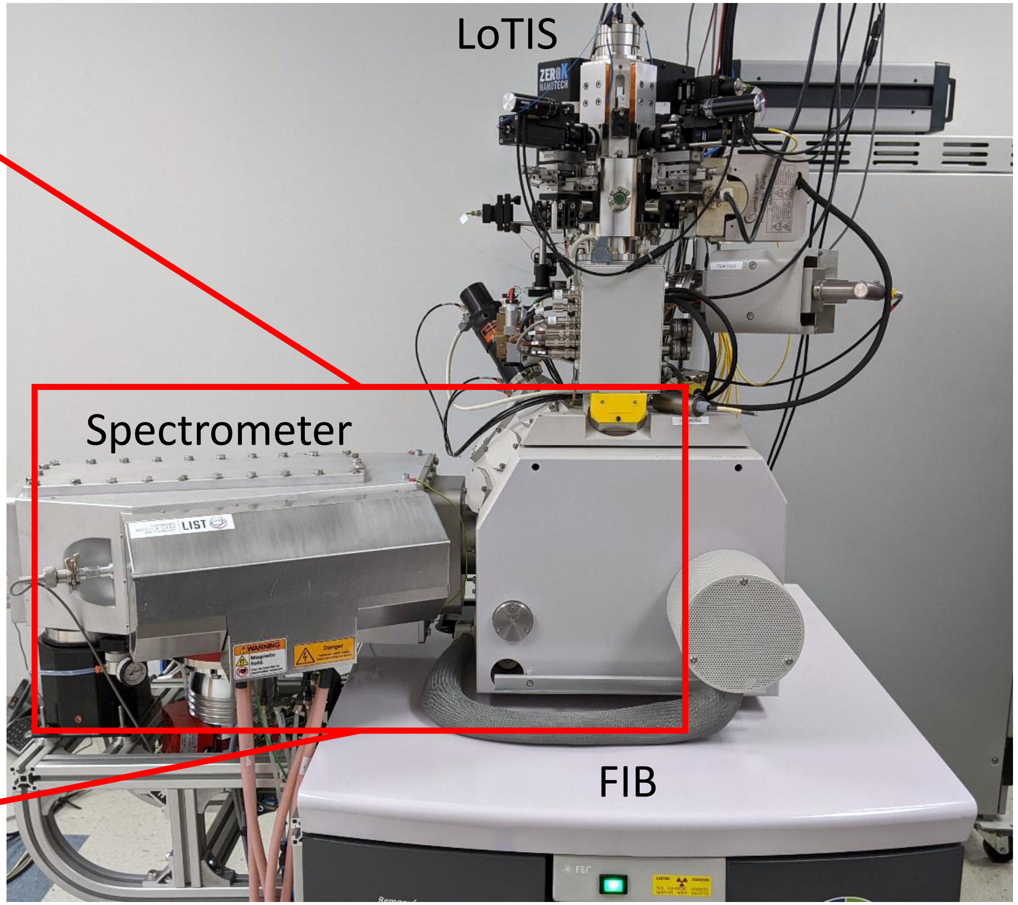
These slides are some of the first public data presented from SIMS:ZERO

SIMS:ZERO

Instrument Overview

Cs+ FIB:ZERO (zeroK) and SIMS spectrometer (LIST: Luxembourg Institute of Science and Technology) on a 600 series FIB (FEI)





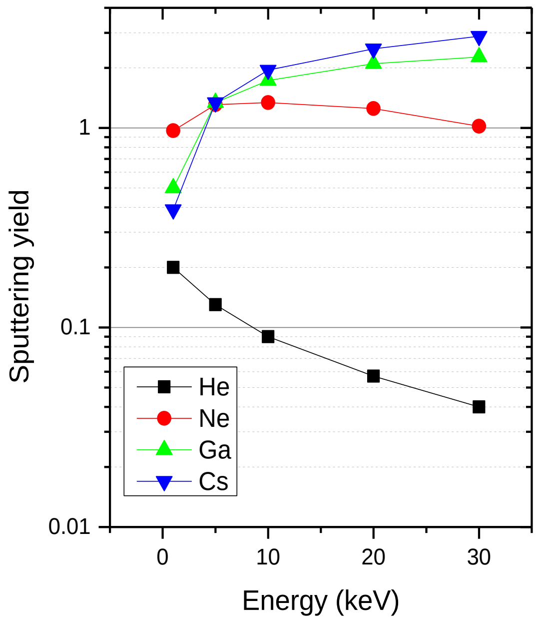
- FIB online 6/2020
- SIMS online 5/2021

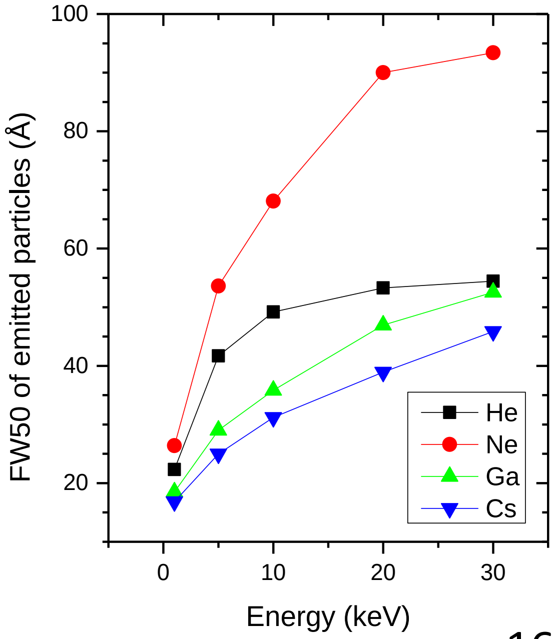
Primary Ion Species Matters

Differing Sputter Rates
→ Analysis Time

Differing interaction Volumes
→ Resolution

Differing Yields
→ Sensitivity Floor, SNR

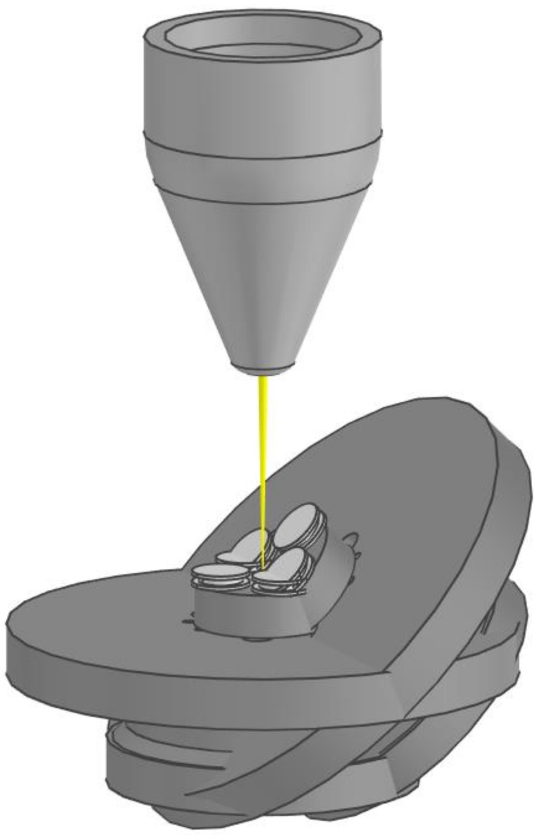




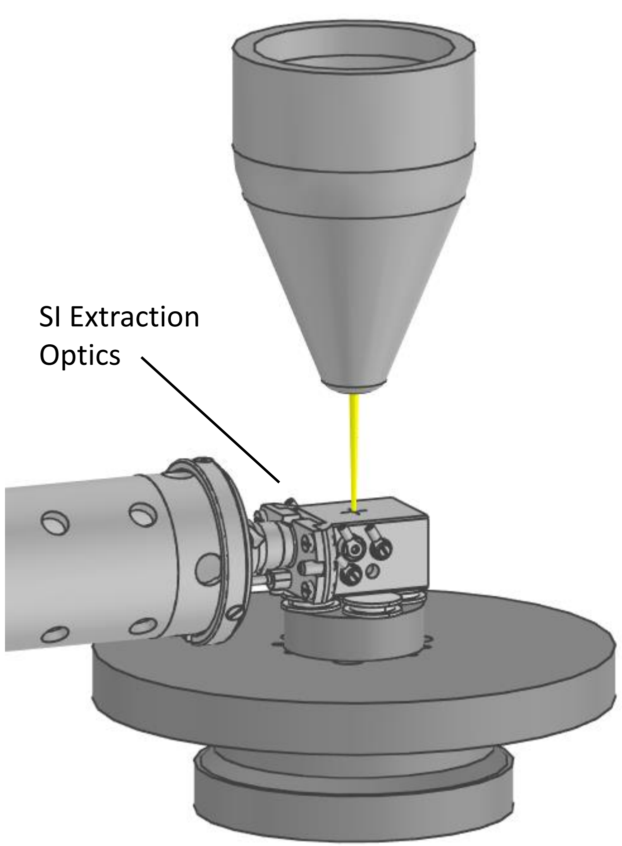
FIB / SIMS Combination

Sample Prep, Nanofabrication / Analysis, Process Control

FIB Mode



SIMS Mode



LoTIS capabilities
- 2-16 keV Cs+ beam
- Up to 5nA beam current
- Spotsize <2nm at low current
- Good spotsizes even at low beam energy

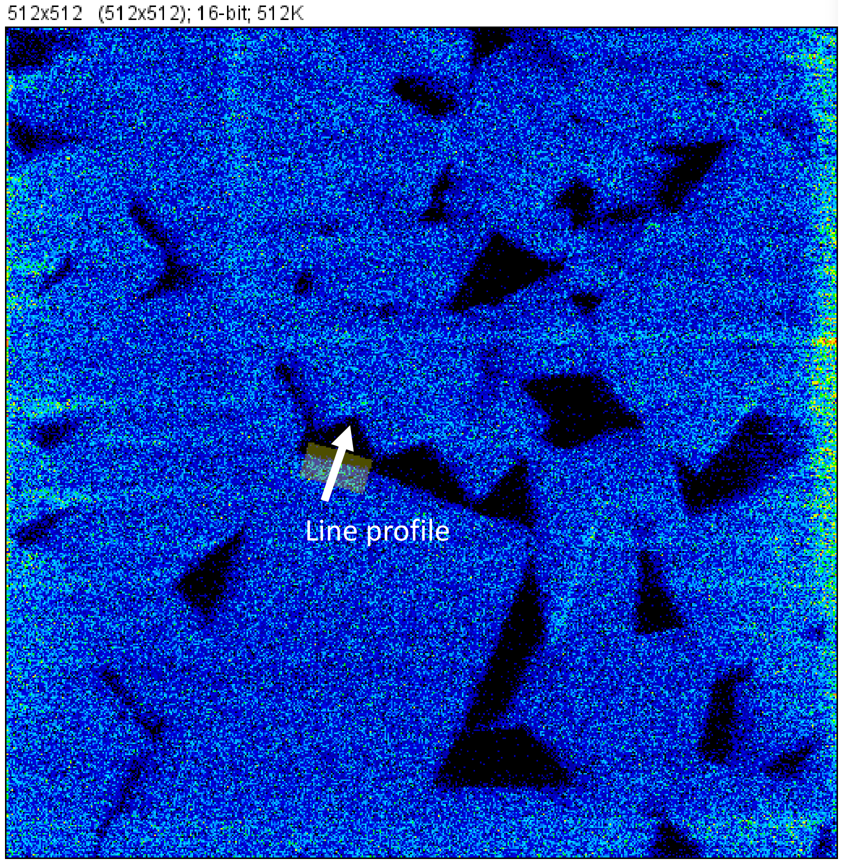
FIB Mode (SIMS Extraction Optics Retracted)
- Milling
- Sample Preparation (eg Sectioning, Polishing)
- Nanofabrication
- Gas-assisted processes (eg Platinum Deposition)
- Tilt stage

SIMS Mode (SIMS Extraction Optics Inserted)
- Highest spatial resolution SIMS imaging
  - $\sigma = 6$ nm demonstrated
- Mass resolution $M/\Delta M = 400$
- Mass range up to 300 amu
- High secondary ion throughput (~40% simulated)
- 4-Channel Detector Standard (Continuous Focal Plane Detector available)

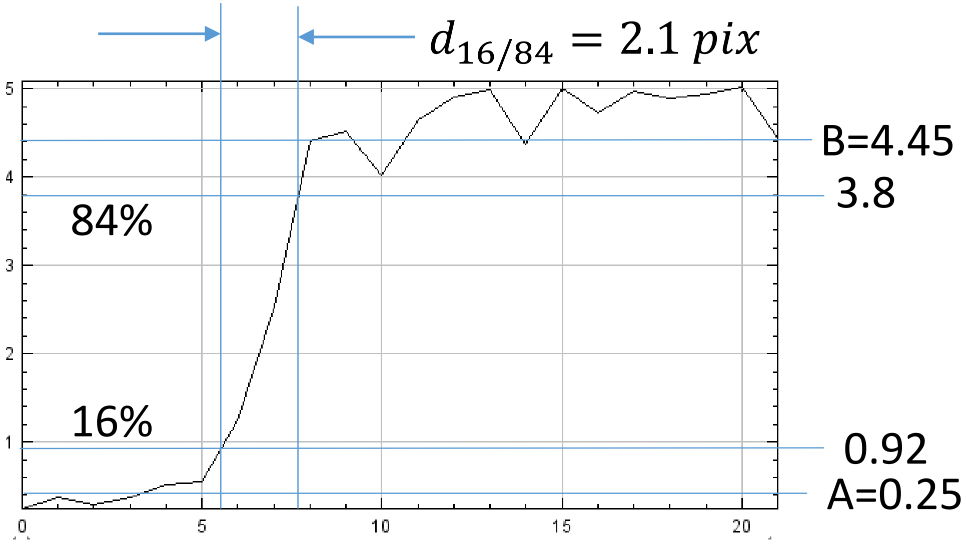
SIMS:ZERO Resolution

Tungsten Carbide

- **SIMS:ZERO can provide higher resolution SIMS scans than any other instrument**
- SIMS resolution is a function of abundance, yield, and spot size
- SIMS:ZERO has a focused ion beam with <3 nm spot size, and since it's Cs^+ we achieve high yields for many materials
- In samples with high abundances, resolution at near the physical limits of SIMS can be achieved (see right)



Multi_WC_2105121624015_CH1.TIF



$$d_{16/84} = 2.97\ \mu m * \frac{2.1}{512} = 12.2\ nm$$

$$\boldsymbol{\sigma = 6.1 nm}\ \textbf{(!)}$$

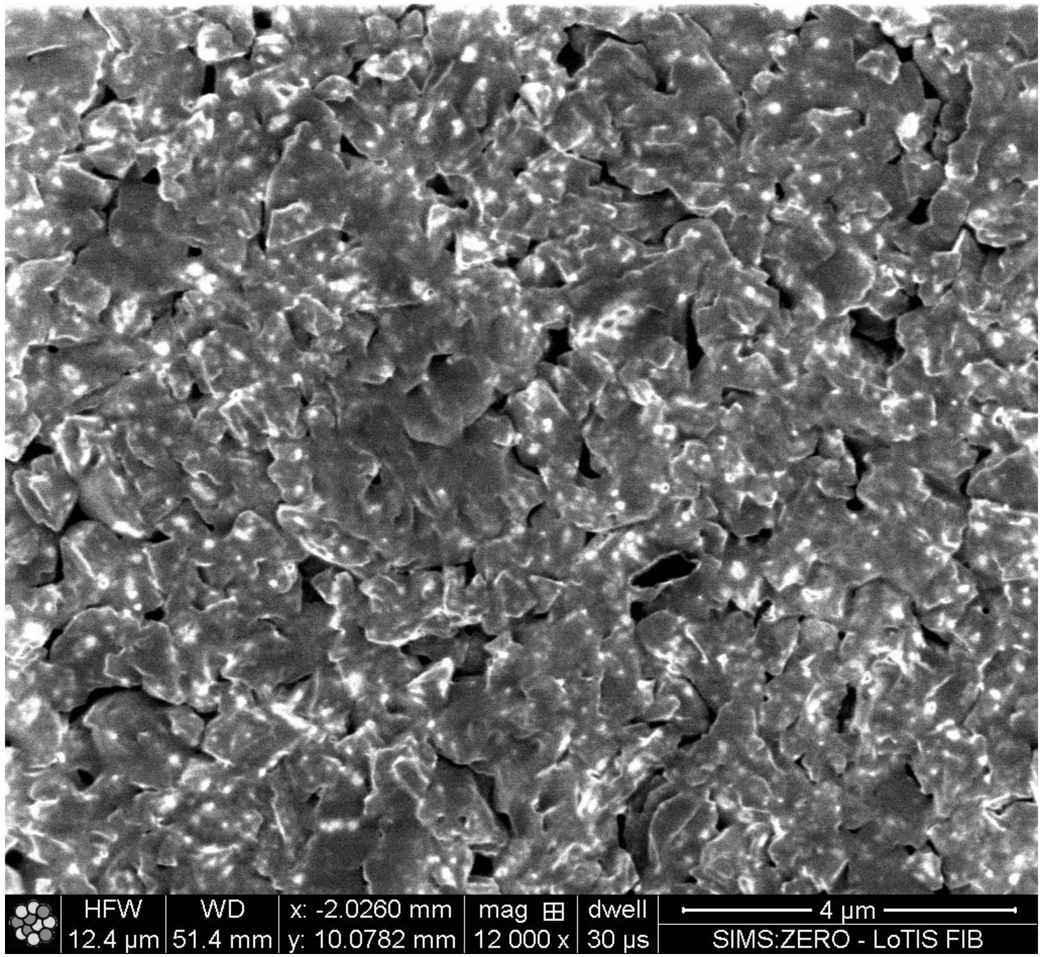
Working Distance = 51.6mm
272s acquisition time.

Negative Ions

Date	05/12/2021
Sample	WC (184 amu)
FOV (um)	2.97um
I (pA)	2.5
U (kV)	16

SIMS Analysis Example

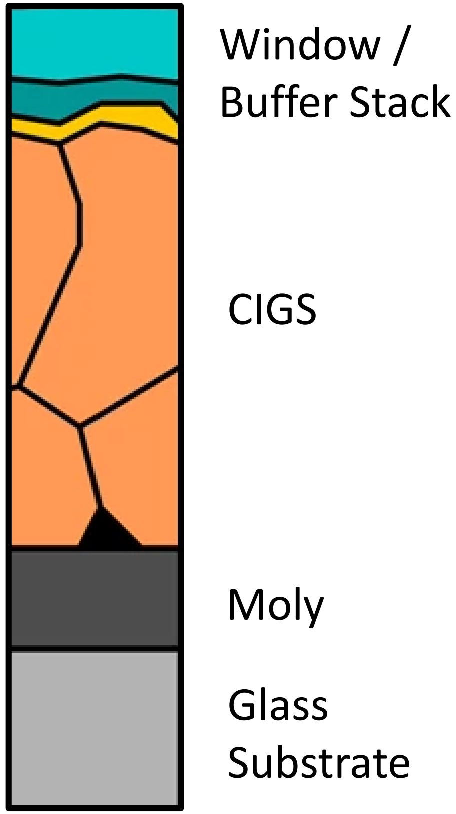
CIGS $Cu(In,Ga)Se_2$ – Rb doped



SE Image Cs+, 16keV, 10pA, 51.6mm WD

Summary

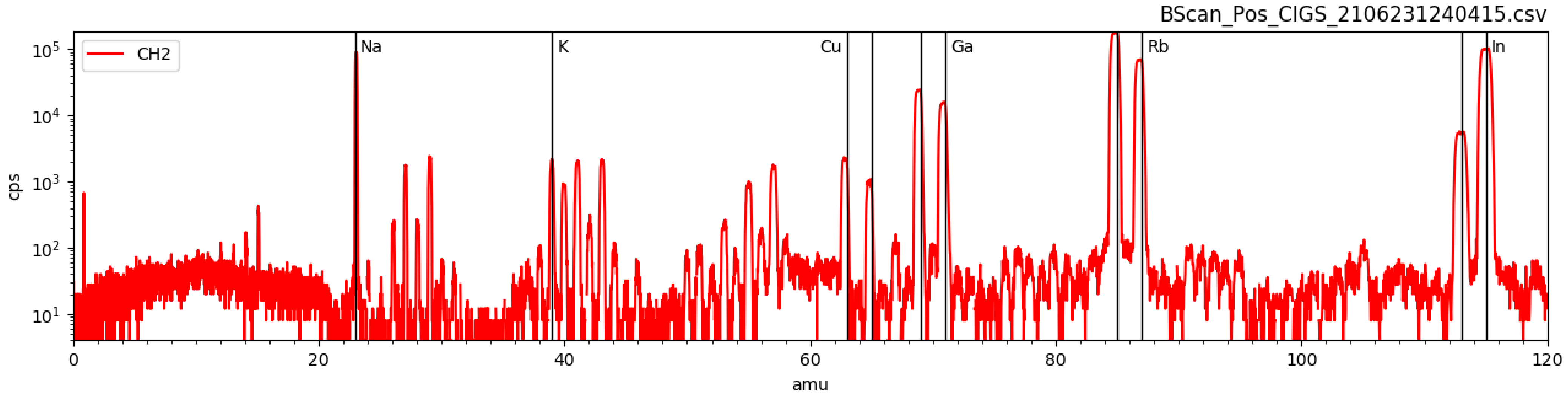
- CIGS is a solar cell absorber material
  - Rubidium doping increases conversion efficiency
- SIMS spectra clearly show all CIGS elements:
  - Cu, In, Ga, Rb in Positive Mode
  - Se in Negative Mode
- Secondary ion imaging channels show distribution of elements in sample, eg Rb dopants concentrated in grain boundaries
- Secondary electron images provide complementary information at high resolution
- Section view technique provides superior SIMS data

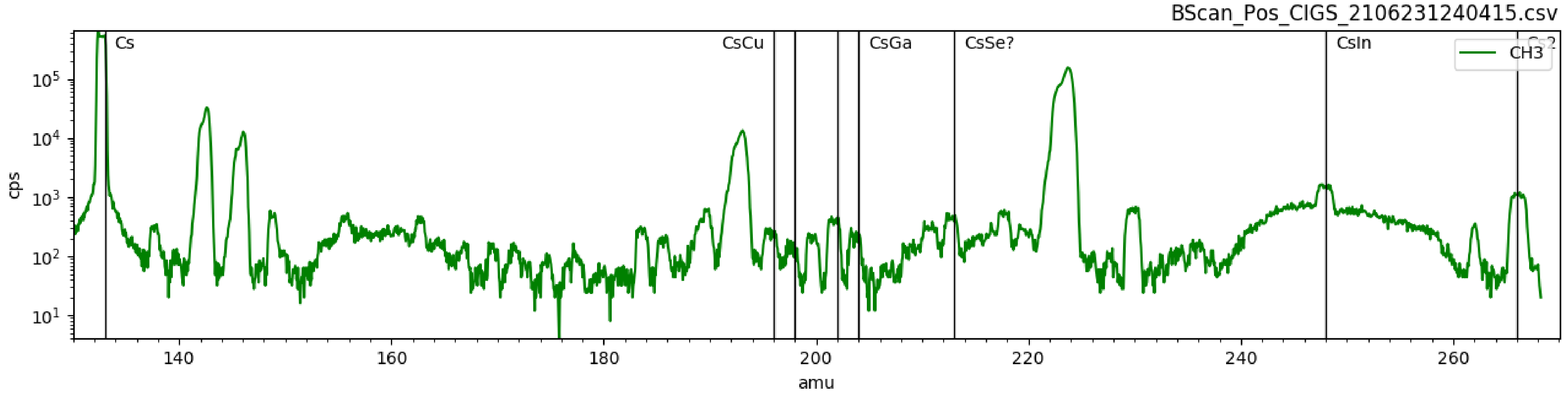


Werner, et al. *Scientific Reports* **volume 10**, 7530 (2020)

CIGS $Cu(In,Ga)Se_2$ – Rb doped

Mass Spectra – Positive Ions



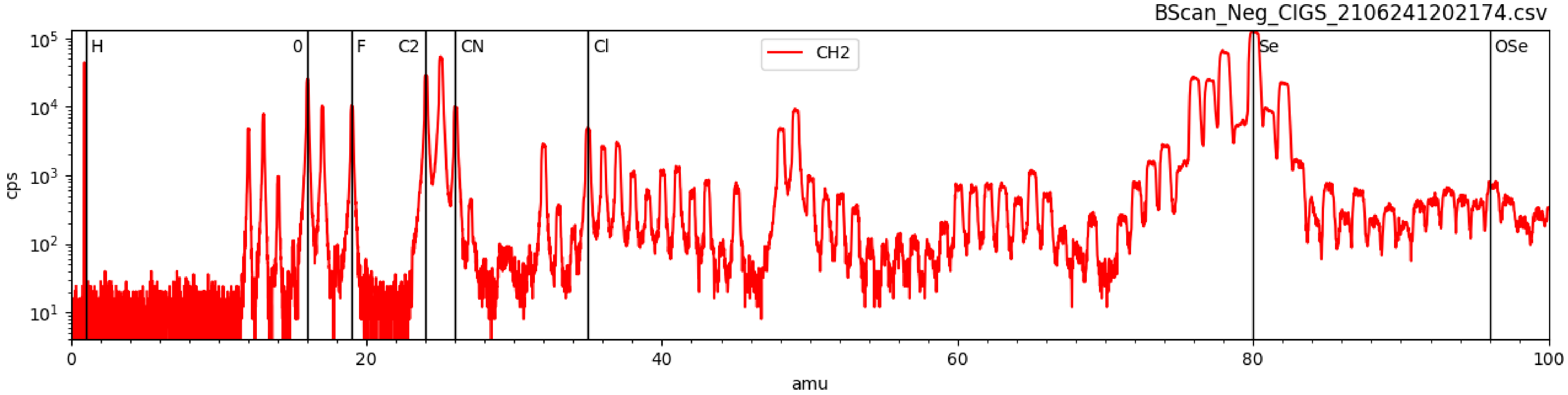


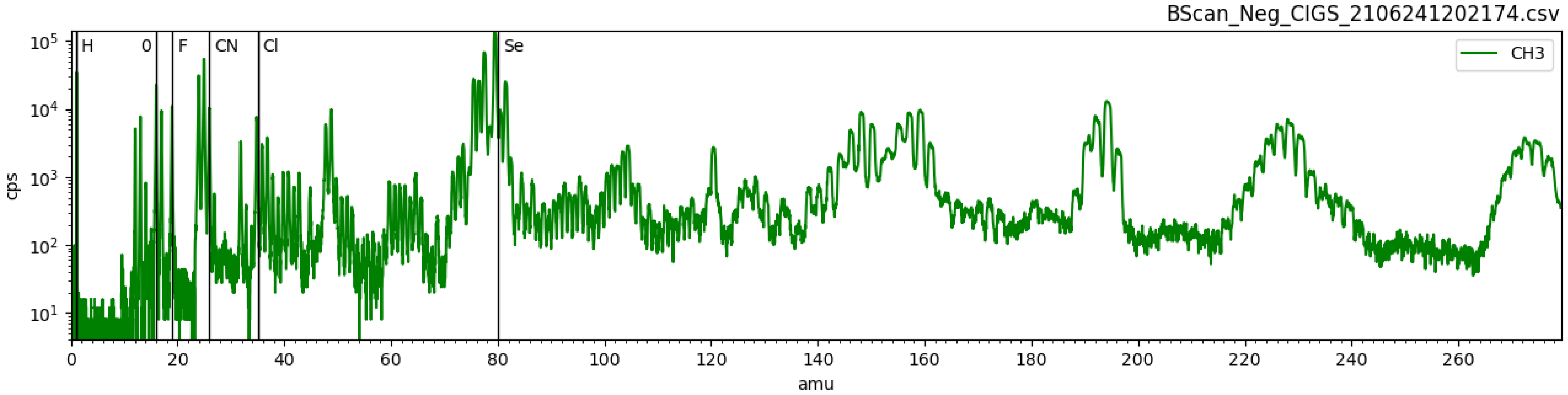
Start (mT) : 30.000000
Stop (mT) : 700.000000
Delta (mT) : 0.100000
Sampling rate (ms) : 250.000000
Waiting time (s) : 0.250000
Period of beam acq : 0
Pos CH1 : 100.000675
Pos CH2 : 200.000362
Pos CH3 : 299.999717
Pos CH4 : 390.000000

Date	06/23/2021
Sample	CIGS
Aperture Slit	100um
FOV (um)	43
I (pA)	10
U (kV)	16

CIGS $Cu(In,Ga)Se_2$ – Rb doped

Mass Spectra – Negative Ions



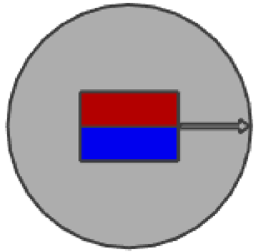


Start (mT) : 30.000000
Stop (mT) : 700.000000
Delta (mT) : 0.100000
Sampling rate (ms) : 250.000000
Waiting time (s) : 0.250000
Period of beam acq : 0
Pos CH1 : 100.000675
Pos CH2 : 200.000362
Pos CH3 : 299.999717
Pos CH4 : 390.000000

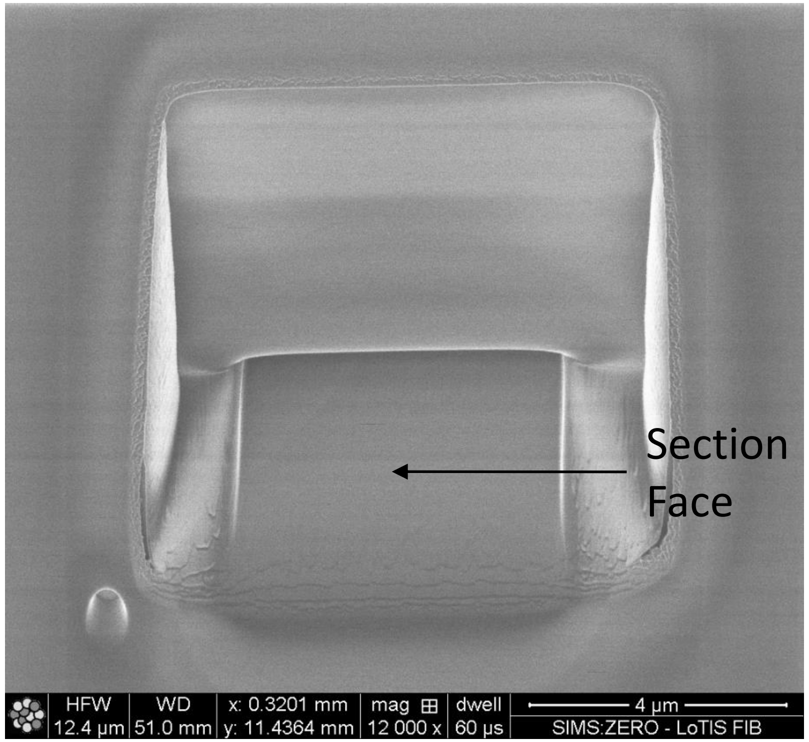
Date	06/24/2021
Sample	CIGS
Aperture Slit	100um
FOV (um)	43
I (pA)	10
U (kV)	16

SIMS-Compatible Section View

45° Angle Cut - Example



View with Sample Normal to Beam; Ready for SIMS on Section



For many samples, working with a section view is a sensible choice

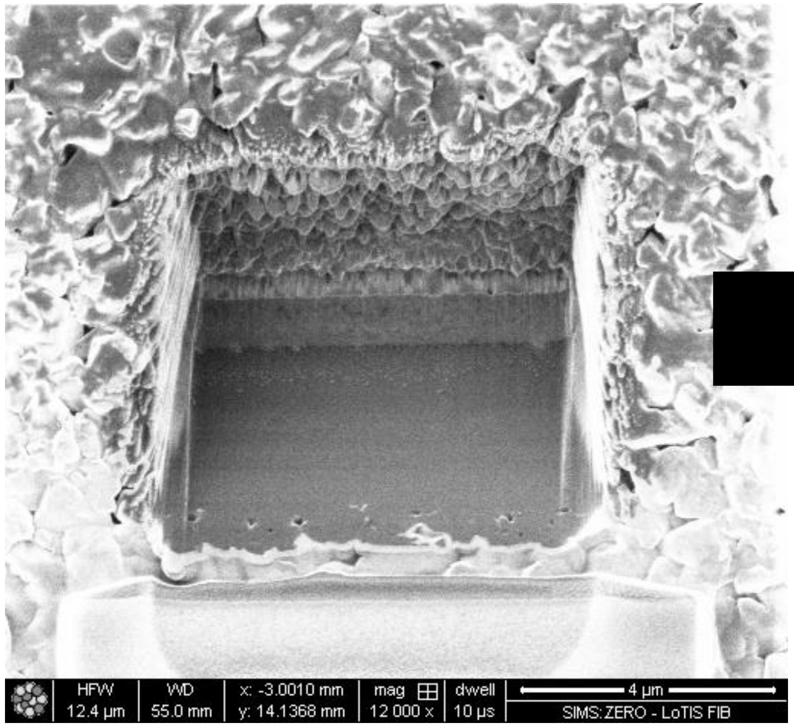
1. Reveal sub-surface structure
2. Obtain depth profile data without accumulated topography from uneven sputtering
3. Polish rough samples to isolate elemental from topographical contrast
4. Build 3D tomographic reconstructions through serial sectioning/polishing

In SIMS:ZERO, sample must be normal to ion beam in SIMS Mode, so section face is cut at 45° to sample surface

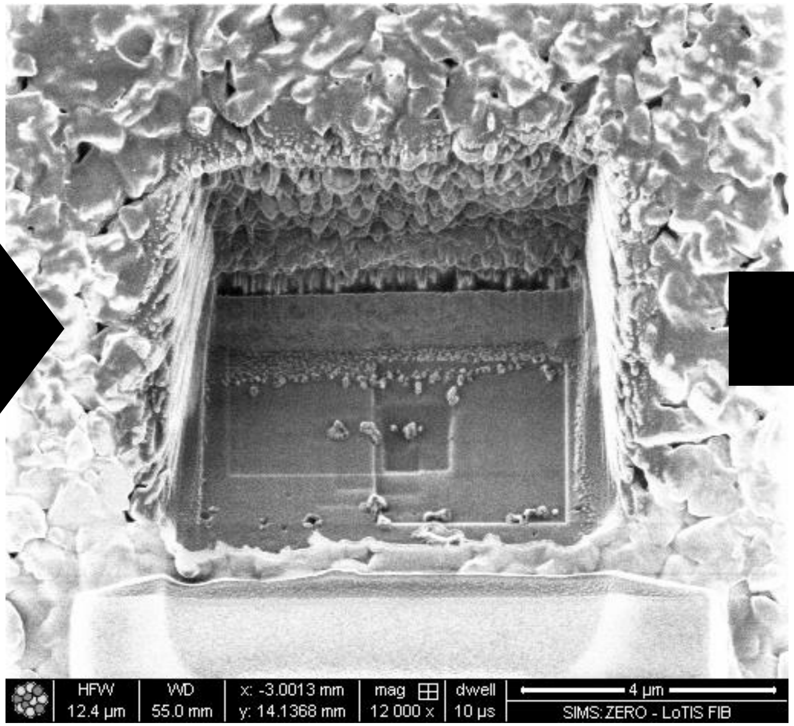
CIGS $Cu(In,Ga)Se_2$ – Rb doped

Serial Sectioning / Imaging / Polishing Work-Flow

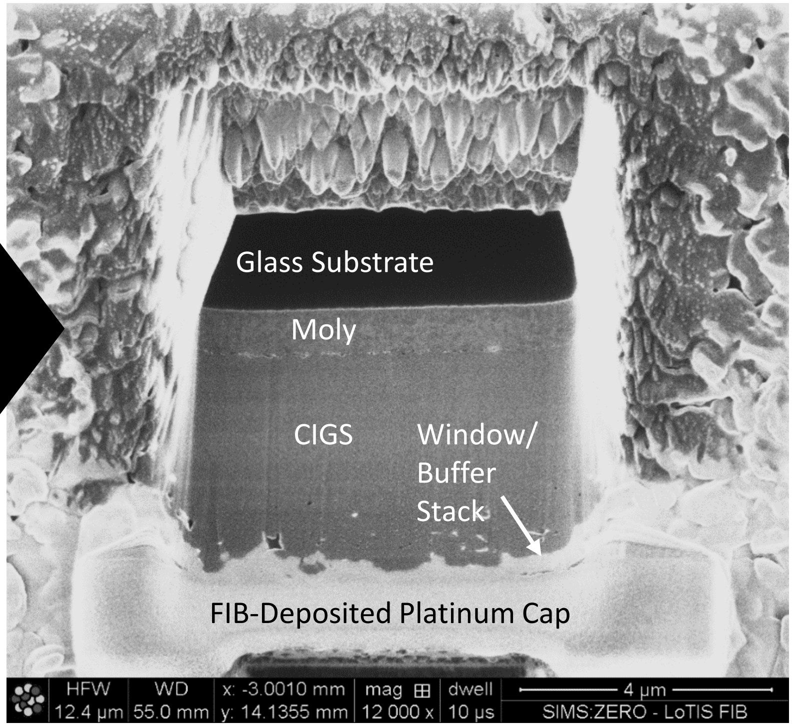
SE Images



SIMS section, prepared with low surface topography, reveals layer structure (glass, moly, CIGS, Window/Buffer Stack)



After SIMS Imaging, section face develops topography which obscures elemental contrast / distribution information



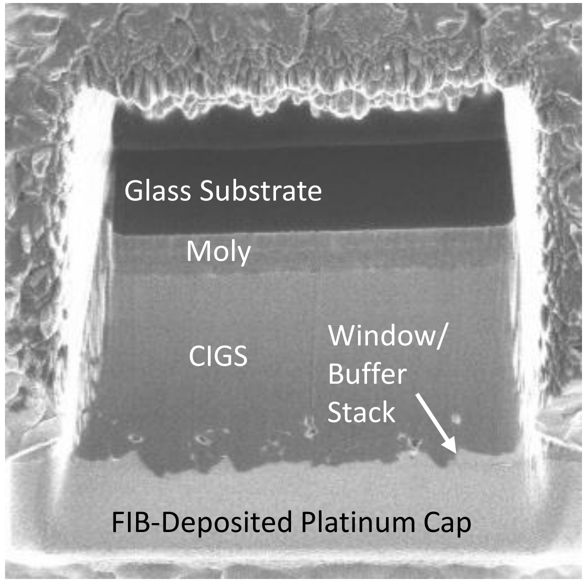
Section face after cleanup mill. Ready for SIMS on next layer

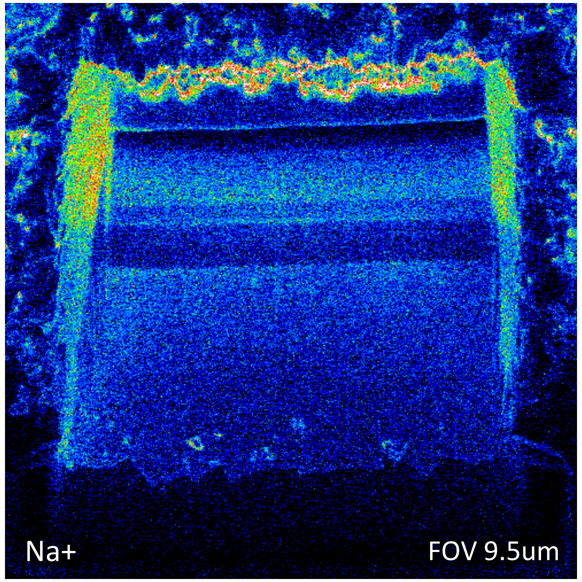
Cs+, 16keV, 10pA, 51.6mm WD

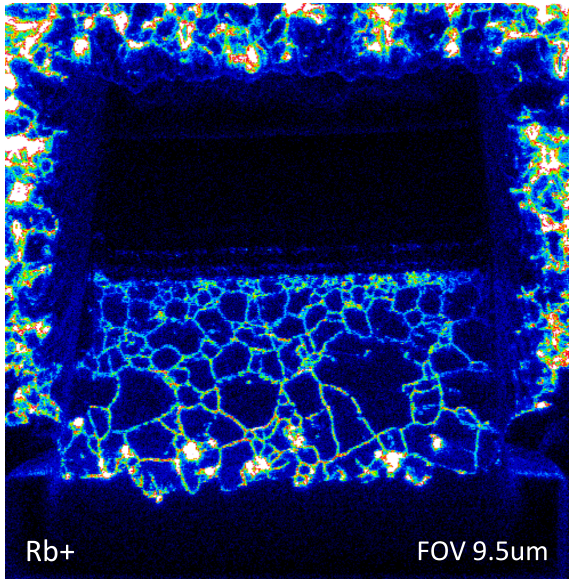
CIGS $Cu(In,Ga)Se_2$ – Rb doped

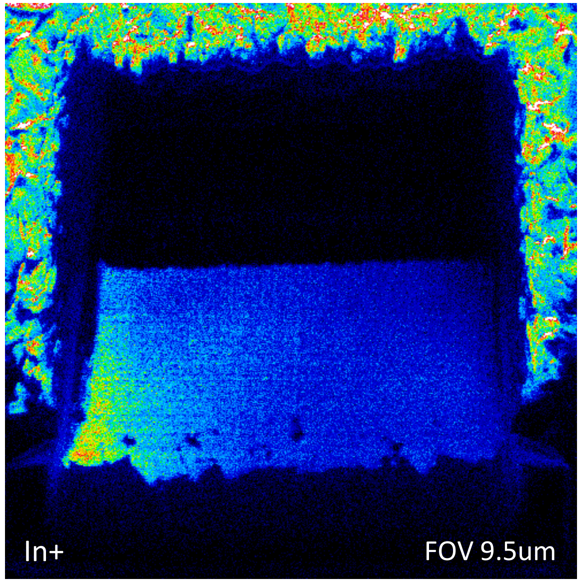
Section View – Positive Ions

SE Image – Pre-SIMS







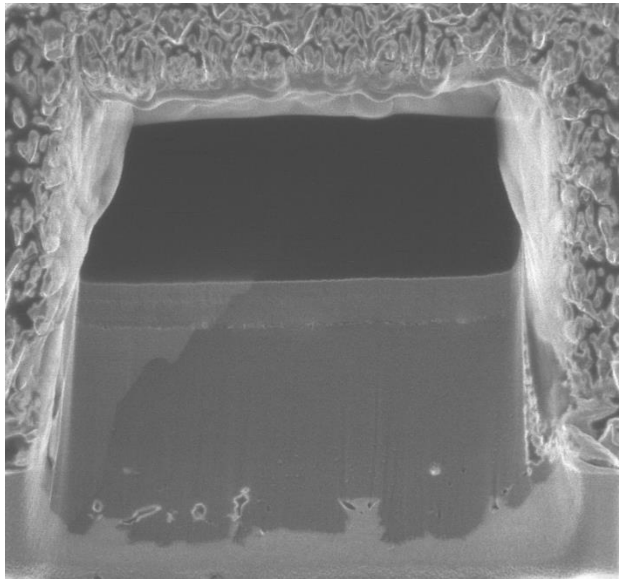


- Rb confined to grain boundaries
- Grains are smaller near the interfaces

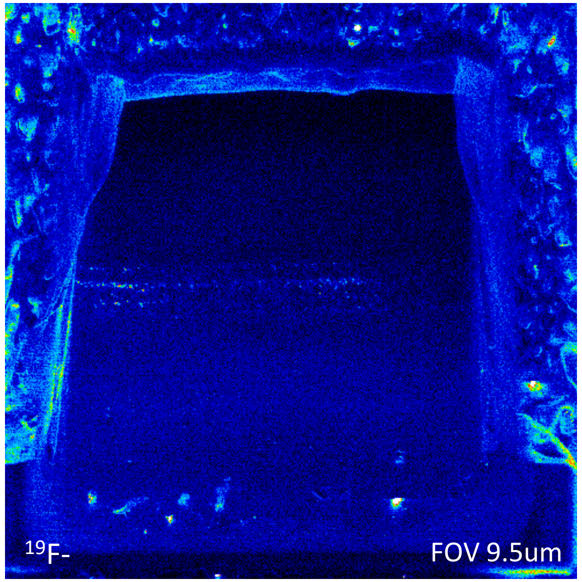
Cs+, 16keV, 3.5pA, 51.6mm WD
CIGS_Pos_2107161606287.csv
CIGS_Pos_2107161613425.csv

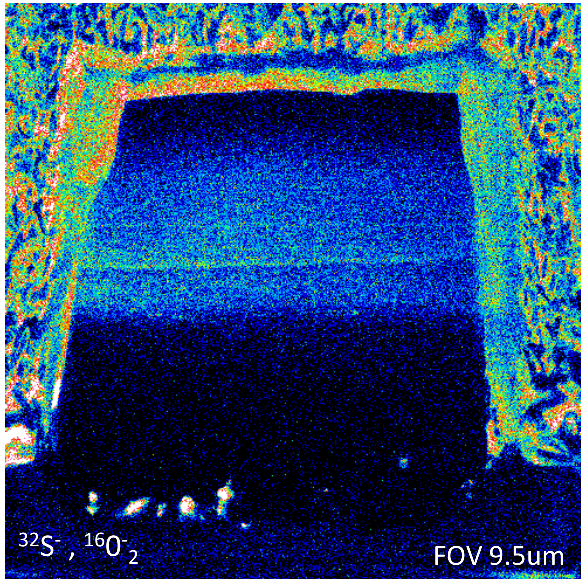
CIGS $Cu(In,Ga)Se_2$ – Rb doped

Section View – Negative Ions – Post 2nd Polish

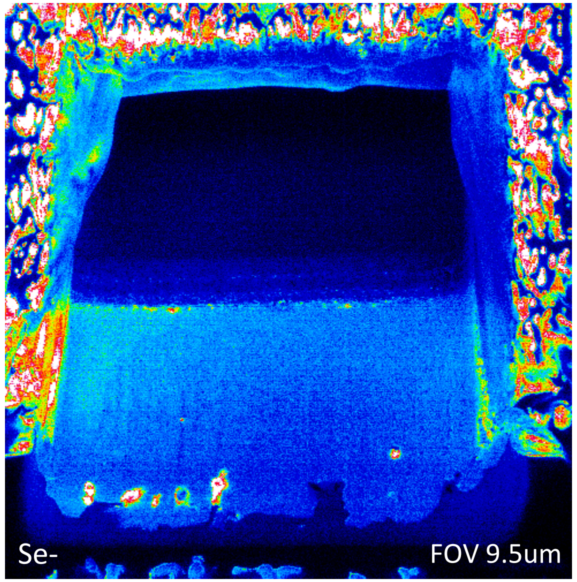


SE Image – Post Polish
Low topography restored





Signal band in CIGS layer near moly may be sulfur, commonly used in CIGS fabrication process; inclusions near surface

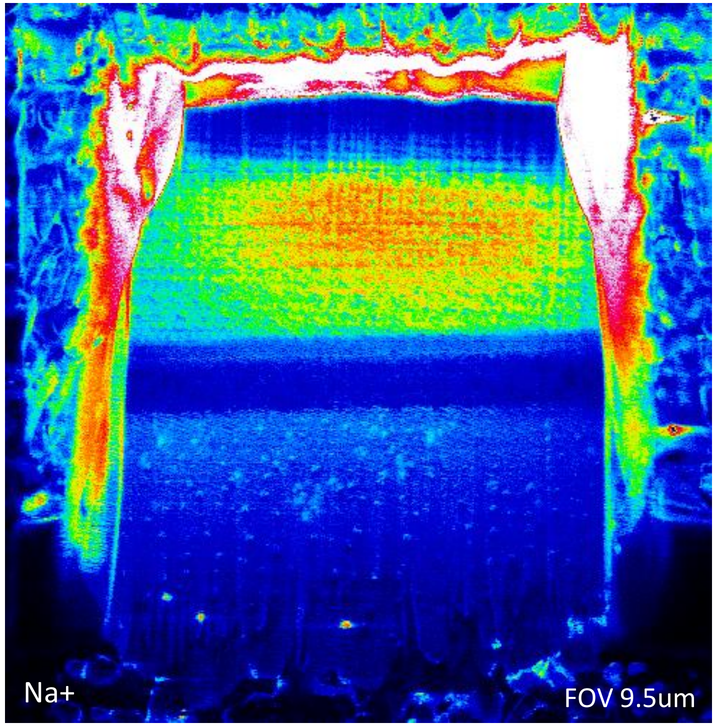


Se is more uniformly distributed in CIGS layer; droplets at moly interface, a few inclusion near surface

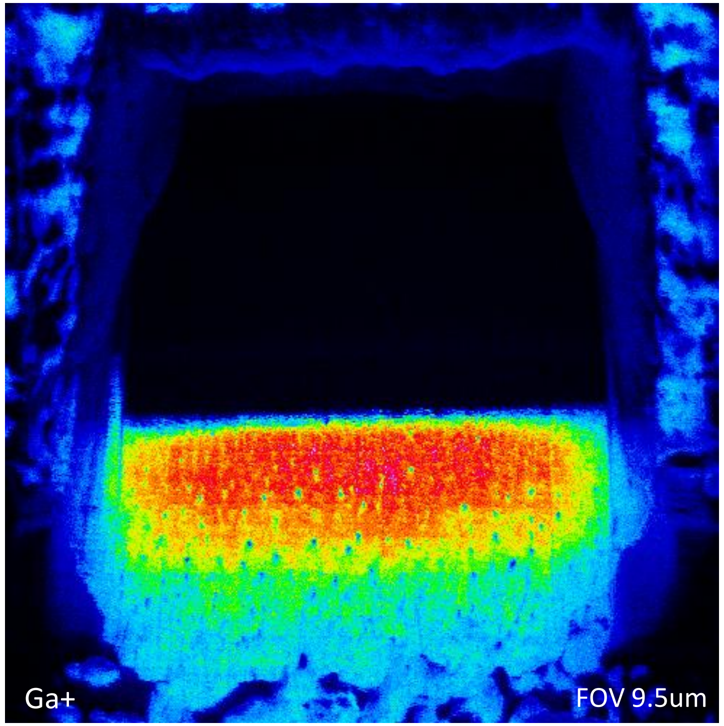
Cs+, 16keV, 10pA, 51.6mm WD
CIGS_Neg_2107201513310.csv

CIGS Cu(In,Ga)Se_2 – Rb doped

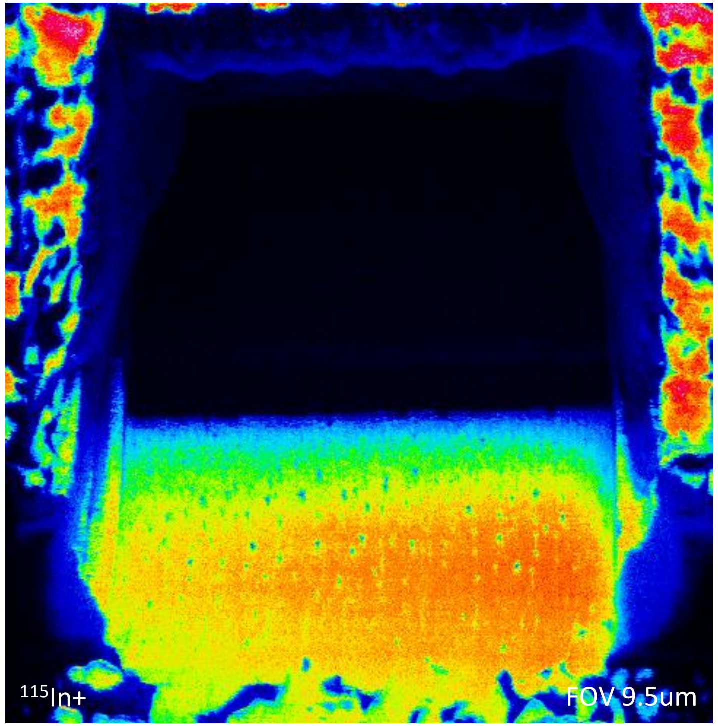
Section View – Positive Ions – Post 3rd Polish



Na – Soda Lime Glass



Ga concentration gradient ↑

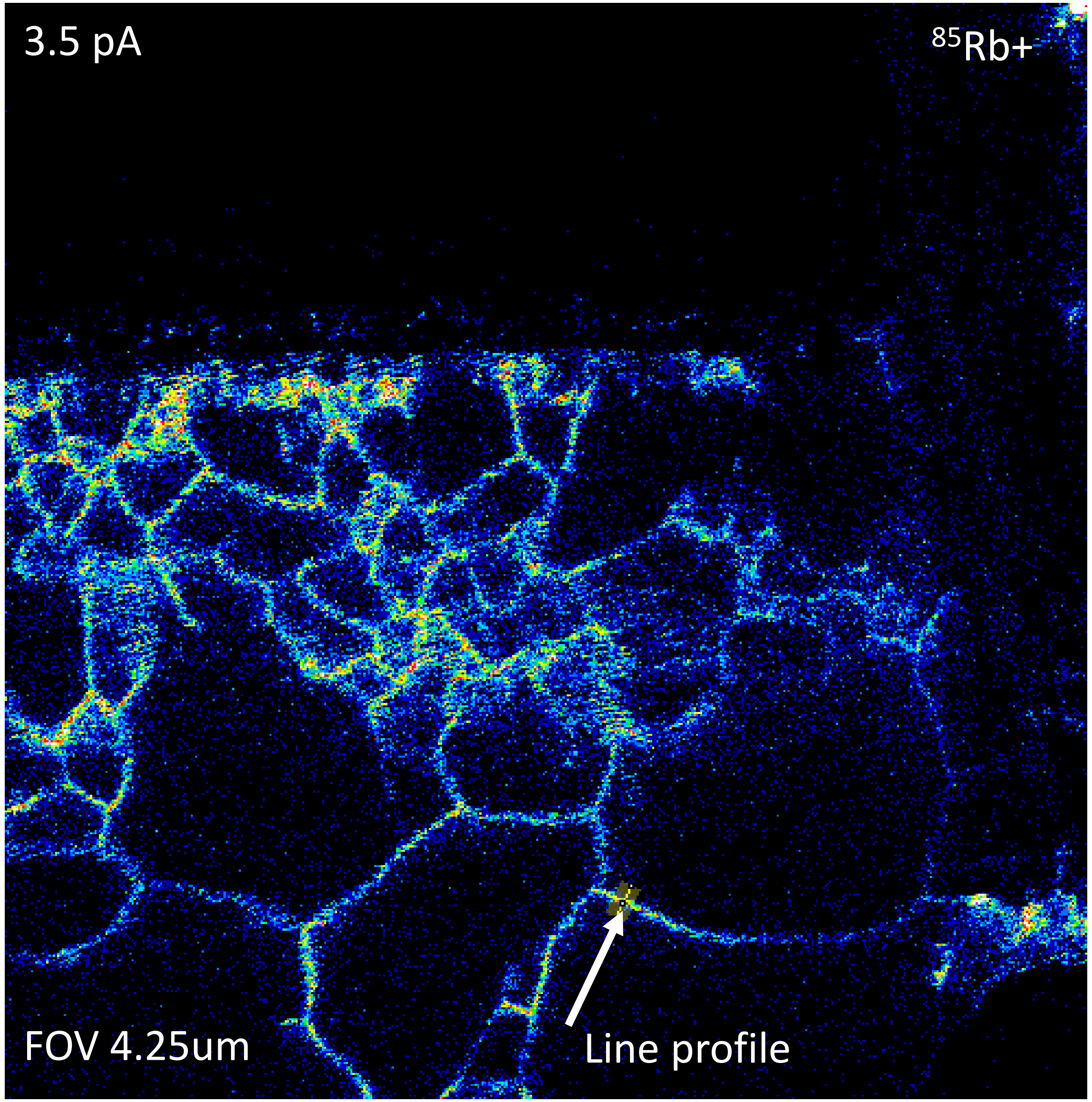


In concentration gradient ↓

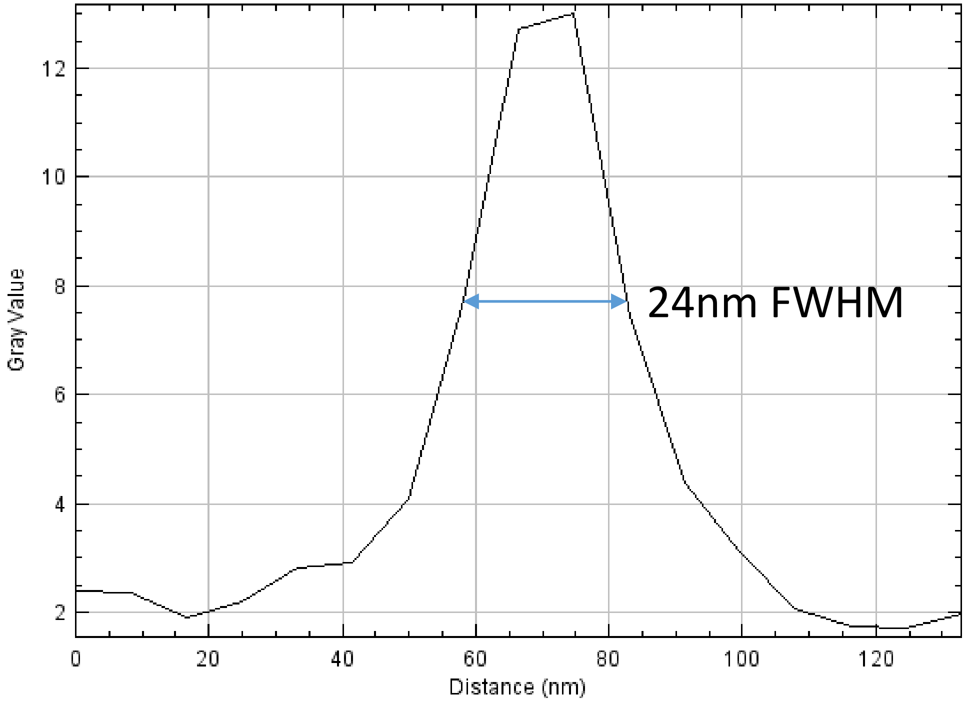
Cs+, 16keV, 10pA, 51.6mm WD
CIGS_Pos_2107201626359.csv

CIGS $Cu(In,Ga)Se_2$ – Rb doped

Section View – Positive Ions



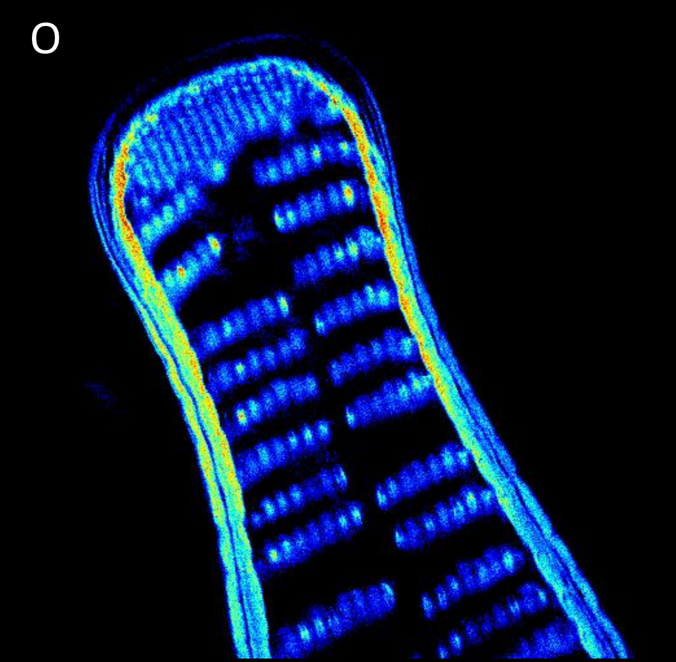
Apparent width of Rubidium signal between grains

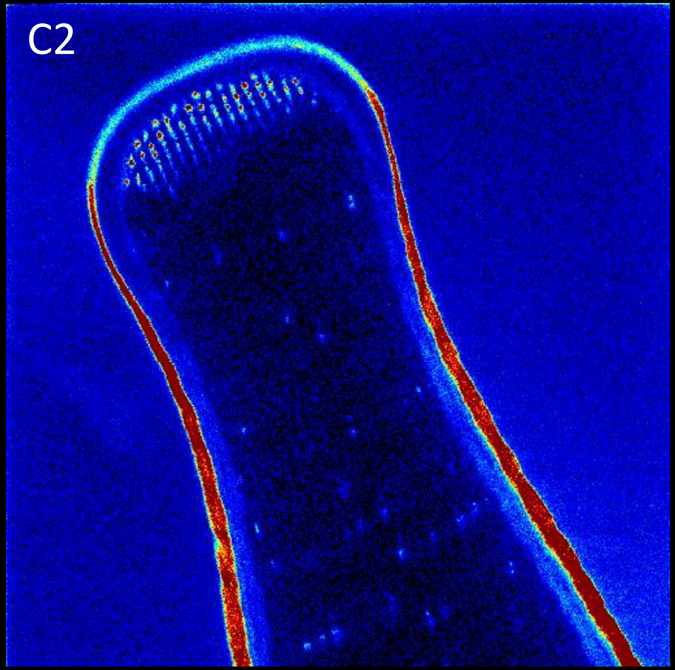


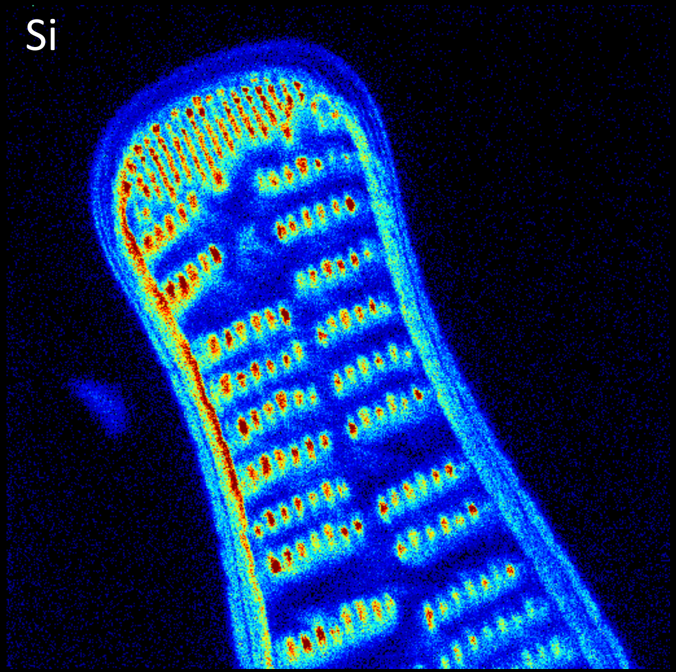
Cs+, 16keV, 3.5pA, 51.6mm WD
CIGS_Pos_2107151409368.csv

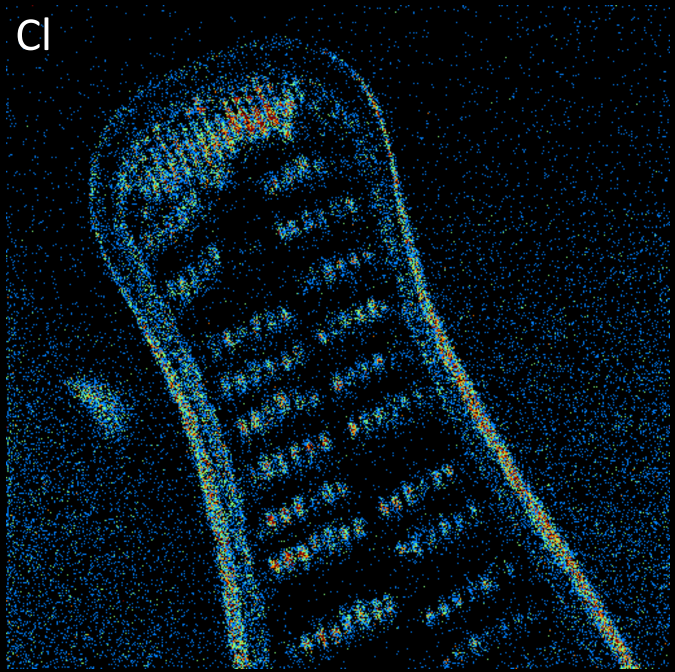
Diatoms (Silica –shelled algae)

7.5 um FoV

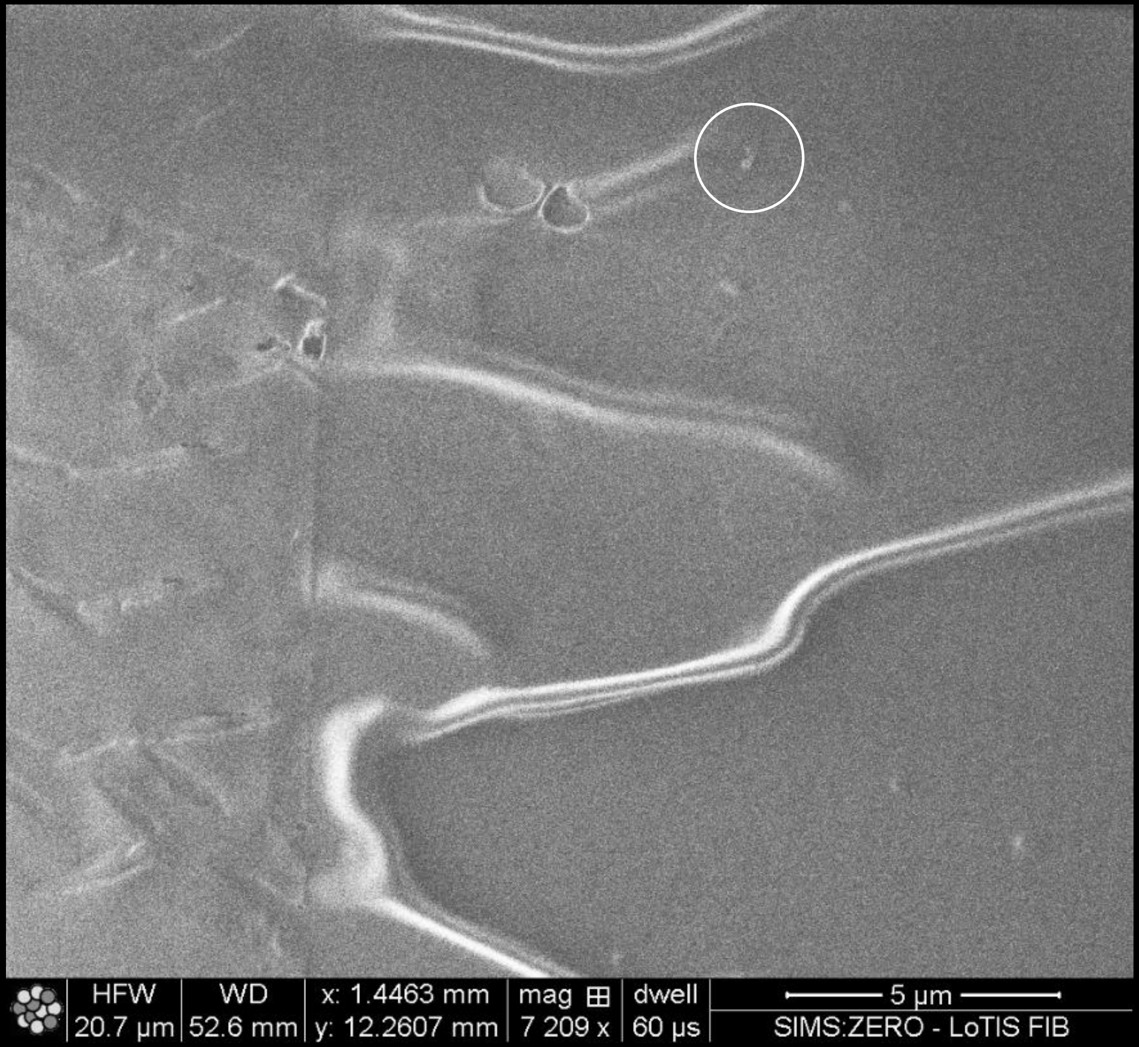


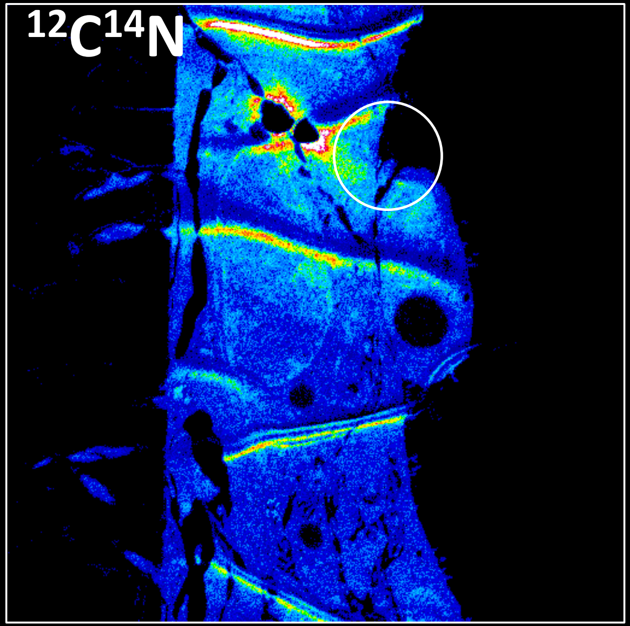






Location of TiO nanoparticle within in huge, fixed cell





Application Example:
SIMS:ZERO as EDX Alternative

EDX elemental analysis is capable of few-nm resolution and can image the majority of elements well, but sensitivity is limited to a few tenths of a percent and sample prep is time consuming

Historically, SIMS has offered excellent (ppm) sensitivity but limited lateral resolution

Now, SIMS:ZERO enables creation of elemental maps with both few-nm resolution and excellent sensitivity without lamella preparation

These capabilities also make possible the creation of 3D elemental maps

Existing Workflow - Thin Sample EDX

Load Sample in FIB/SEM → Locate ROI → Prepare Lamella → Transfer to TEM with EDX → Locate ROI → EDX Analysis

Only one shot : analysis limited to a single depth

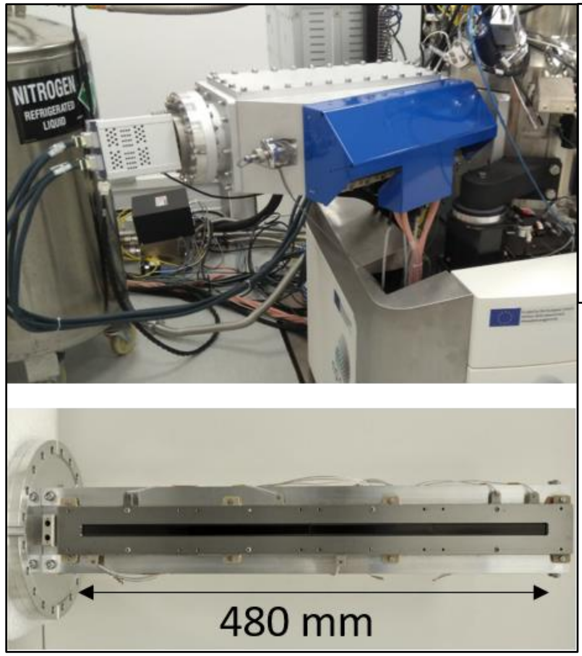
Optimized Workflow - SIMS:ZERO

Load Sample in SIMS:ZERO → Locate ROI → Prepare Cross Section → SIMS Analysis → SIMS Analysis on Deeper Plane → SIMS Analysis on Deeper Plane → SIMS Analysis on Deeper Plane

Continuous Detector

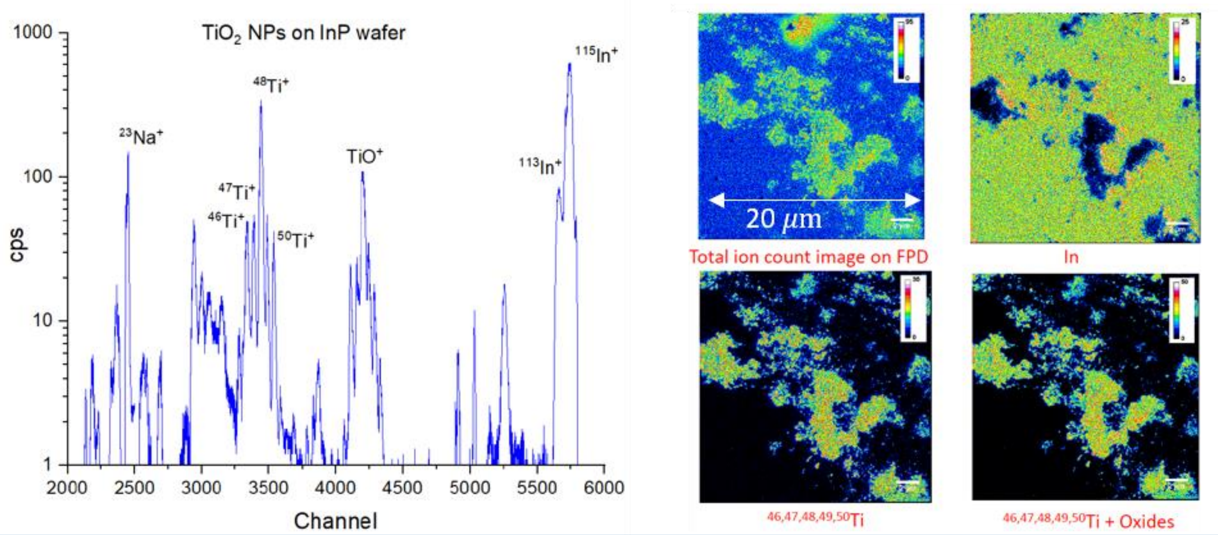
A SIMS:ZERO Option

- SIMS signals for a given element are split into many lines (e.g. Ti, TiO etc..) .
- In discrete-detector systems this leads to a loss of information and lower SNR.
- With continuous detector technology we can sample the entire mass spectrum at once.
- Now we can collect the entire spectrum as in TOF systems, but without painfully long acquisition times.



(Top) Photo of SIMS spectrometer (at LIST) and the continuous focal plane detector mounted to a vacuum flange.

(Bottom) A 480mm micro-channel plate that spans the focal plane of the spectrometer.



Data from by a continuous focal plane detector. Mass spectrum (Left) and surface compositional maps (Right). The sample under interrogation was titanium oxide nanoparticles on an indium phosphide substrate.

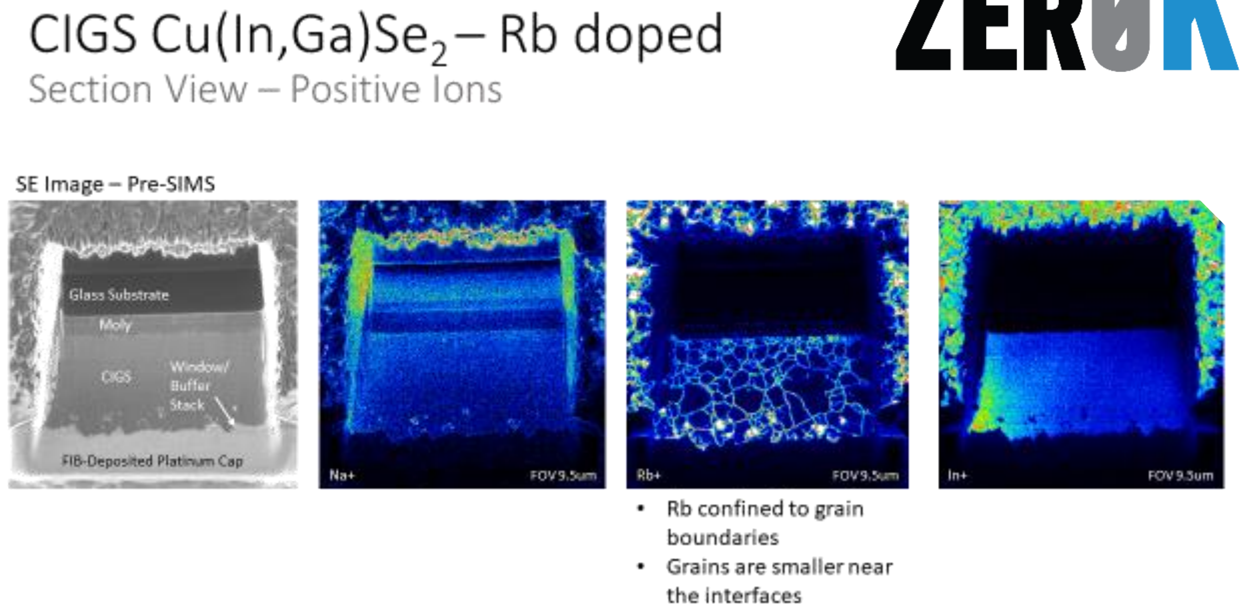
SUMMARY SIMS:ZERO

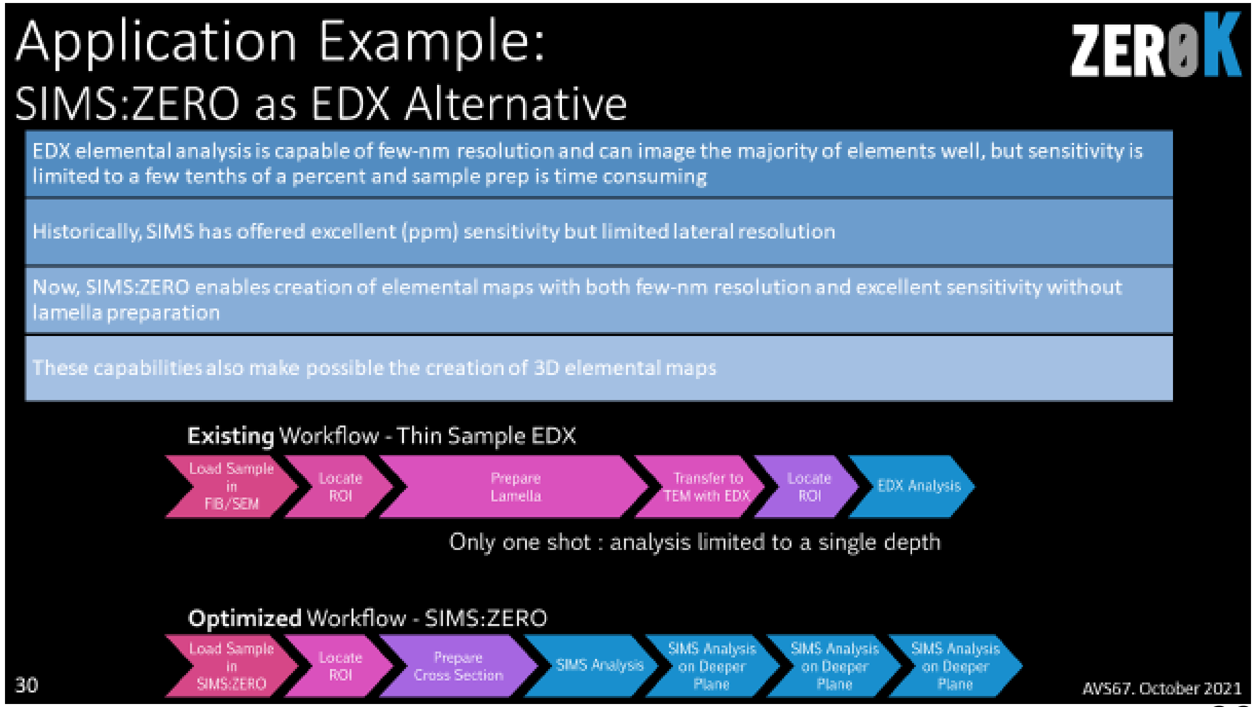
... has all the capabilities of FIB:ZERO

... adds high-resolution, high-sensitivity, high speed elemental analysis

... enables new modes of operation

Slides at right featuring new modes of operation and high resolution elemental mapping summarize the story best





Spot Sizes

Selected Beam Energies and Currents

Results given as a σ

- $d_{50} = 2.2\ \sigma$
- $d_{35-65} = \frac{\sigma}{1.3}$,
- $d_{16-84} = 2\sigma$

Spot sizes are about 2x smaller than Helios (Ga^+) at <10 pA, and at lower energy

Bit worse spot sizes than Zeiss He/Ne, but better machining performance in many cases

Methodology in [1]

[1] A V Steele *et al* 2017 *Nano Futures* **1** 015005
Open access link: https://iopscience.iop.org/article/10.1088/2399-1984/aa6a48

16 kV

Current (pA)	Spot Size (1-σ nm)
1.5	<2.0
3.0	2.3
10	4.0
30	7.5
100	23
300	57
1000	175
5500	580

8 kV

Current (pA)	Spot Size (1-σ nm)
1.5	2.3
3	2.5
10	4.7
30	7.6
100	55
300	150
1000	244
2600	510

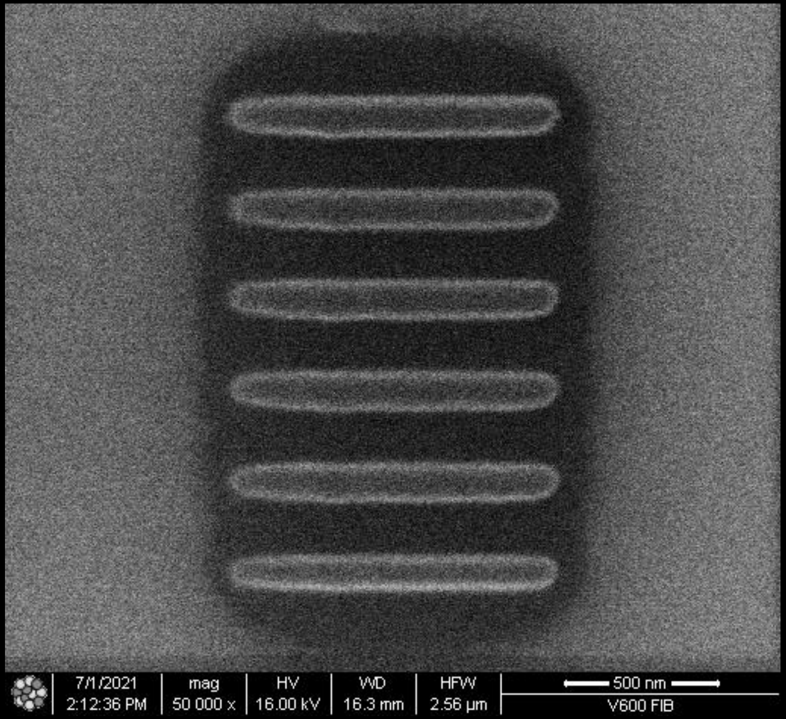
Low-Energy

Energy (kV)	Current (pA)	Spot Size (1-σ nm)
5	3.5	15
2	3.5	44

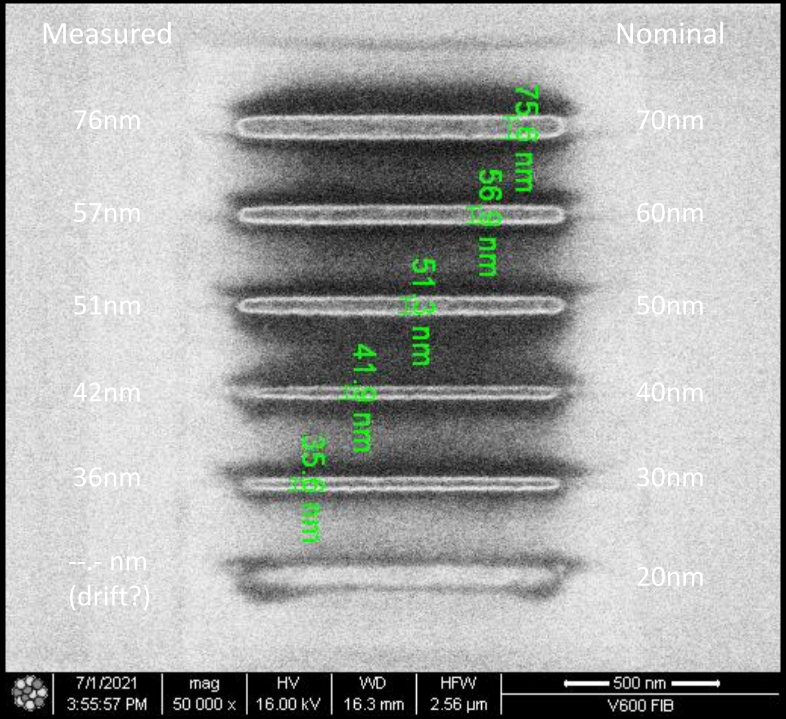
Platinum Deposition – Narrow Lines

→ FIB:ZERO can provide very narrow metal lines

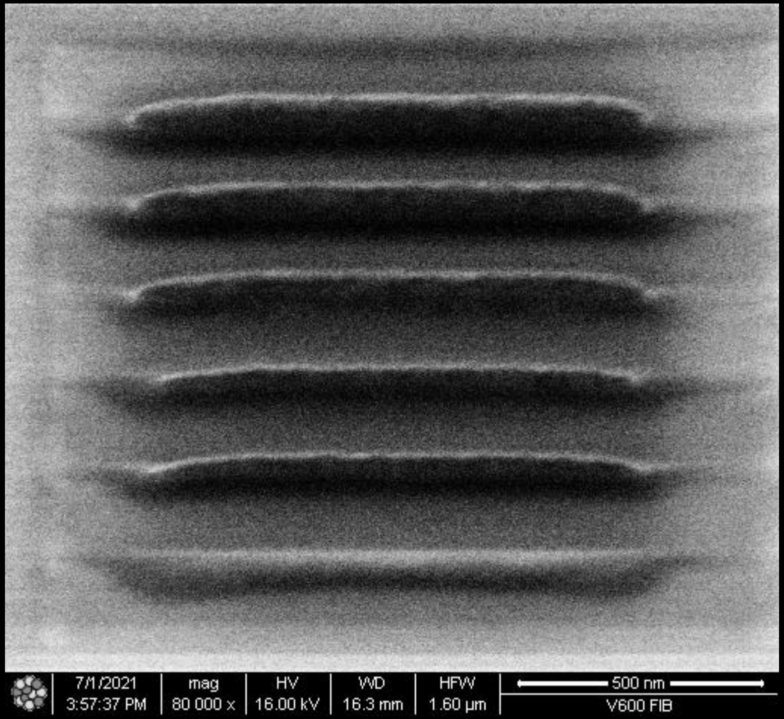
Pt lines with 100nm width as deposited on Si.



Pt lines after cleanup mill.



Tilted view to show height of Pt lines above Si substrate.



Deposition, milling, and imaging performed with 1.0pA Cs+ ion beam.